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**TITAN III
STORABLE
PROPELLANT
HANDBOOK**

JUNE 1961

XEROX



Prepared By: **BELL AEROSYSTEMS COMPANY, DIVISION OF BELL AEROSPACE CORPORATION**
BUFFALO, NEW YORK

For: **AIR FORCE FLIGHT TEST CENTER, EDWARDS AIR FORCE BASE, CALIFORNIA**

TITAN II STORABLE PROPELLANT HANDBOOK

Final Handbook

**BELL AEROSYSTEMS COMPANY
Division of Bell Aerospace Corporation
Buffalo 5, New York**

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Project Engineer**

Report No. 8111-933003

**Contract No. AF04(611)-6079
Project 6753
Task 30282**

JUNE 1961

**AIR FORCE FLIGHT TEST CENTER
Edwards Air Force Base
California**

FOREWORD

This is the third and final report prepared for the Air Force Flight Test Center by the Bell Aerosystems Company under Contract AF04(611)-6079, "Storable Propellant Data for the Titan II Program," Project 6753 and Task 30282. Mr. C.F. Emde (FIRLP) of AFFTC was Program Manager and Mr. Glen W. Howell of the Space Technology Laboratories, Los Angeles, California, was Coordinator. Mr. Ralph R. Liberto, Project Engineer of Bell Aerosystems, directed the study effort. Research under this contract started on 15 June 1960 and ended on 15 April 1961. Results of the effort are reported in this handbook. At a later date, a revision to this handbook will be prepared as part of the task under Contract AF04(647)-846.

Harold W. Stafford
Technical Editor

ABSTRACT

Summarized are the physical properties, materials compatibility, handling techniques, flammability and explosivity, and procedures for storing, cleaning, and flushing of the Titan II propellants, N_2C_4 as the oxidizer and a nominal 50/50 blend of UDMH and N_2H_4 as the fuel. The data presented was derived both from a literature survey and from a test program conducted at Bell Aerosystems Company and at the U.S. Bureau of Mines.

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SYMBOLS/ABBREVIATIONS USED IN THE TEXT

AFBMD	Air Force Ballistic Missile Division
AFFTC	Air Force Flight Test Center
ARDC	Air Research and Development Command
ADL	Arthur D. Little, Inc.
JPL	Jet Propulsion Laboratory
STL	Space Technology Laboratories, Inc.
AEROZINE-50	Trade name adopted by Aerojet-General (Nominal 50/50 blend by weight of UDMH and N ₂ H ₄)
50/50 FUEL BLEND	Nominal 50/50 blend by weight of UDMH and N ₂ H ₄
NO ₂	Nitrogen Dioxide
N ₂ H ₄	Hydrazine, Specification Grade MIL-P-26536A (USAF)
N ₂ O ₄	Nitrogen Tetroxide, Specification Grade MIL-P-26539 (USAF), an Equilibrium Mixture of NO ₂ and N ₂ O ₄
RFNA	Red Fuming Nitric Acid
UDMH	Unsymmetrical Dimethylhydrazine, Specification Grade MIL-D-25604B(ASG)
M.A.C.	Maximum Allowable Concentration
MPY	Mils per Year
ppm	Parts per Million by Volume
RASCAL	Components of the LR-67-BA-9 rocket engine produced by Bell Aerosystems for the GAM-63A (RASCAL) Missile
SIT	Spontaneous Ignition Temperature(s)

Metal and alloy designations used in this handbook, such as type 304SS, are those established by the cognizant agencies and used in the trade.

SECTION 1.0
INTRODUCTION

SECTION 1.0
INTRODUCTION

A storable propellant combination of N_2O_4 as the oxidizer, and a nominal 50/50 blend of UDMH and N_2H_4 as the fuel, has been selected for the Titan II ballistic missile. These propellants were studied by Bell Aerosystems Company and the resultant data on physical properties, materials compatibility, handling, safety, and flammability and explosivity is published in this handbook. The information was compiled from industry and government data and from trade literature. Laboratory tests were conducted to augment available data and to help in analyzing information.

SECTION 2.0
PHYSICAL PROPERTIES OF 50/50 FUEL BLEND

SECTION 2.0

PHYSICAL PROPERTIES OF 50/50 FUEL BLEND

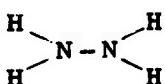
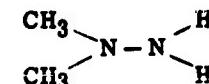
The fuel blend, comprising a 50/50 mixture of UDMH and N_2H_4 , is a clear, colorless, hygroscopic (capable of absorbing moisture readily) liquid having a characteristic ammoniacal odor. When the blend is exposed to air, a distinct fishy odor is evident in addition to the ammonia odor; this is probably caused by the air oxidation of UDMH.

The UDMH and N_2H_4 are miscible in all proportions. When combined, there is an immediate tendency for each to dissolve in the other. However, because of their different densities, they are easily layered; UDMH above the N_2H_4 , especially when UDMH is poured into a vessel containing N_2H_4 . Under these conditions, a distinct interface may form (Reference 1).

In the pages that follow, additional physical property data is presented for this fuel blend. The information was obtained from the literature or from laboratory tests conducted at Bell Aerosystems. Table 2.1 summarizes pertinent physical properties of the fuel blend.

The boiling point of the fuel blend listed in Table 2.1 is interpolated from the measured vapor pressure data plotted in Figure 2.4. At the boiling point, the concentration of UDMH in the vapor phase is approximately 92% by weight. At 77°F, the concentration of UDMH in the vapor phase is approximately 95% by weight (Reference 1). During distillation of this blend, a wide temperature range is noted between the point at which 10% by volume is distilled and the 90% by volume is distilled. This temperature difference is 80°F (Table 2.6). This blend is not a constant boiling mixture.

TABLE 2.1
PHYSICAL PROPERTIES OF THE 50/50 FUEL BLEND

	<u>N₂H₄</u>	<u>UDME</u>
Structural Formula of the Fuel		
Molecular Weight (ave)	45.0	
Melting Point ^a	18.8°F	
Boiling Point ^a	158.2°F	
Physical State	Colorless Liquid	
Density of Liquid at 77°F ^a	56.1 lb/ft ³	
Viscosity of Liquid at 77°F ^a	54.9 x 10 ⁻⁵ lb/ft-sec	
Vapor Pressure at 77°F ^b	2.75 psia	
Critical Temperature (calc)	634°F	
Critical Pressure (calc)	1696 psia	
Heat of Vaporization (calc)	425.8 BTU/lb	
Heat of Formation at 77°F (calc)	527.6 BTU/lb	
Specific Heat at 77°F (calc)	0.604 BTU/lb-°F	
Thermal Conductivity at 77°F (calc)	0.151 BTU/ft-hr-°F	

a - Measured on samples of the fuel blend of typical composition
(51.0% N₂H₄, 48.2% UDMH, and 0.5% H₂O).

b - Fuel blend composition 51.0% N₂H₄, 48.4% UDMH, and 0.6% H₂O.

(Reference 1)

2.1 FUEL BLEND SPECIFICATION

A tentative specification, MIL-P-27402(USAF), is available for the 50/50 fuel blend. This specification contains a method for performing analyses to fulfill the chemical requirements given in Table 2.2. This method is the salicylaldehyde method which is based upon a differential titration and determines UDMH directly and N₂H₄ indirectly. Water content and other soluble impurities are calculated by difference.

TABLE 2.2
PROPELLANT SPECIFICATION - 50/50 FUEL BLEND

Chemical Requirements	Specification (wt %)
UDMH	47.0 (min)
N ₂ H ₄	51.0 ±0.8
Total N ₂ H ₄ and UDMH	98.2 (min)
H ₂ O and Other Soluble Impurities	1.8 (max)

2.2 MELTING POINT

Figure 2.1 contains melting point data for various mixtures of UDMH and N_2H_4 obtained from JPL, Aerojet-General Corporation, and Bell Aerosystems Company. The Bell and Aerojet data for the fuel blend composition agree. The melting point of the fuel blend, as estimated by Aerojet, can range from about 17° to $21^{\circ}F$, thereby meeting the composition requirements of the procurement specification (see Table 2.2).

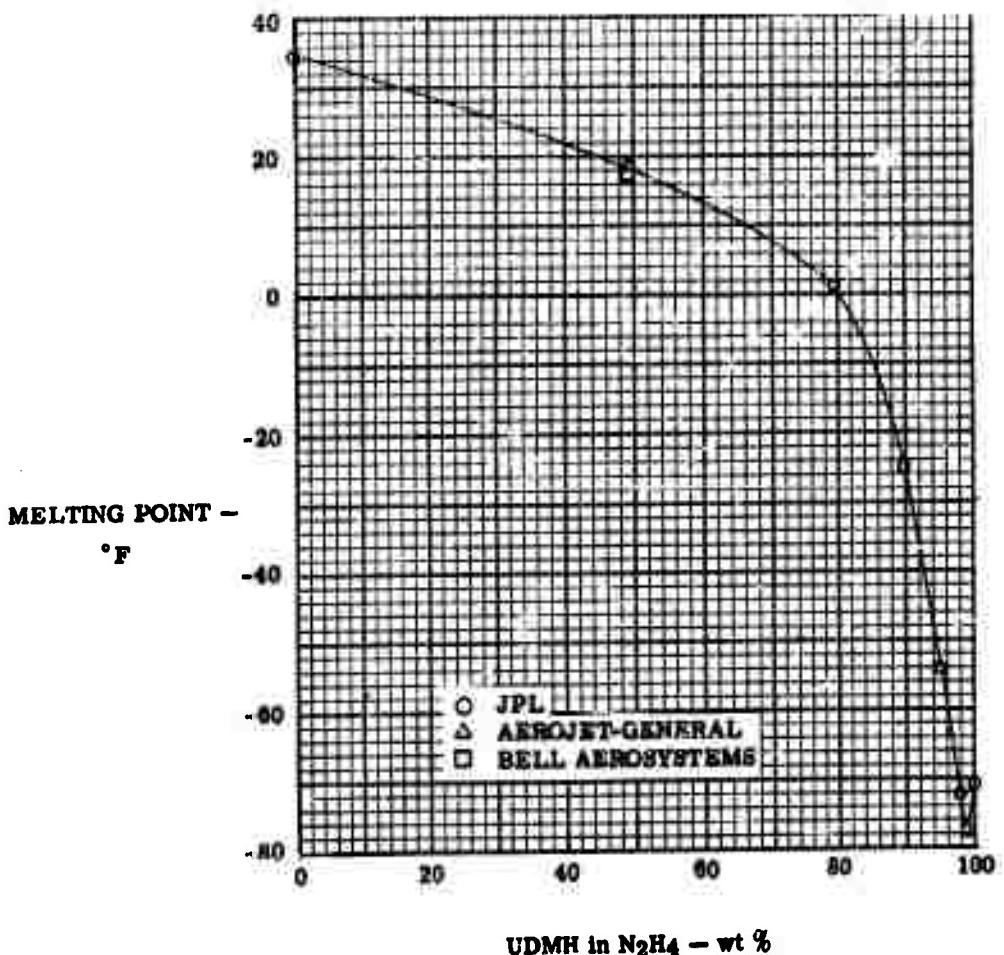
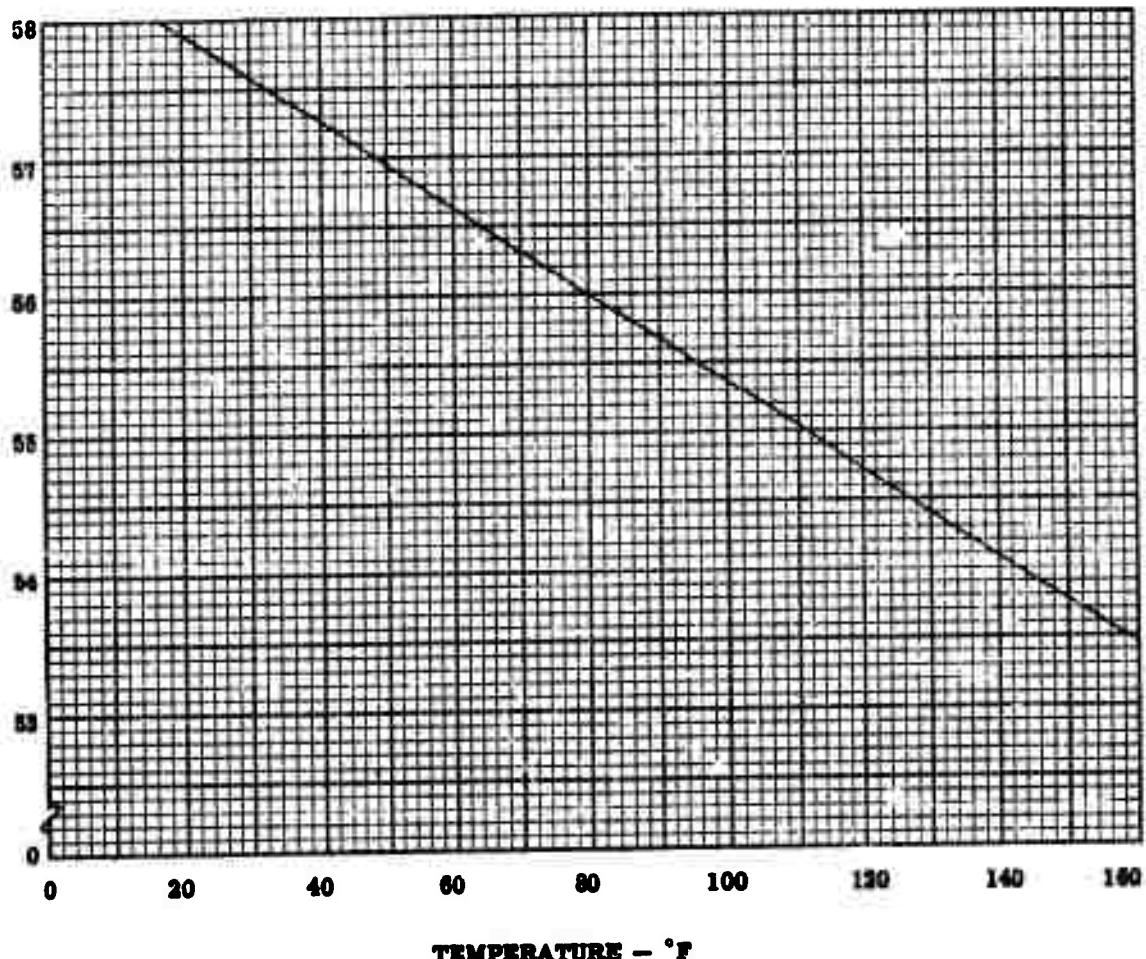


Figure 2.1. Melting Point vs Percent Weight of UDMH in N_2H_4

2.3 DENSITY

Figures 2.2 and 2.3 present density and specific gravity data for the fuel blend as reported by Aerojet-General Corporation (Reference 1).

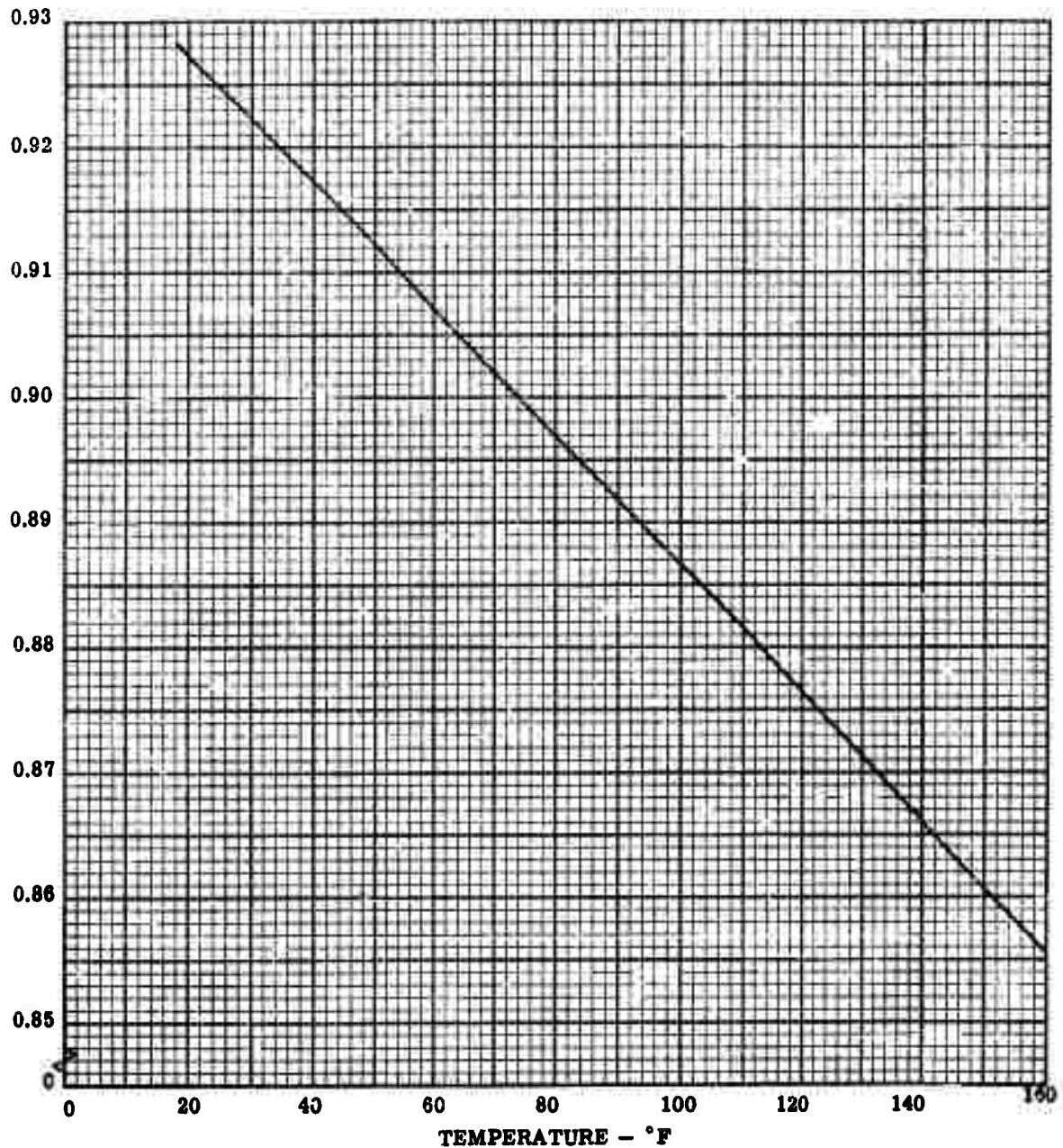
DENSITY - lb/cu ft



(Reference 1)

Figure 2.2. Density of 50/50 Fuel Blend

SPECIFIC GRAVITY



(Reference 1)

Figure 2.3. Specific Gravity of 50/50 Fuel Blend

2.4 VAPOR PRESSURE

This fuel is a mixture of UDMH and N_2H_4 , with UDMH possessing the higher vapor pressure. The vapor pressure of a liquid mixture depends upon the composition of the mixture and is the sum of the partial pressures of each gas at a constant temperature. However, as one of the more-volatile components vaporizes from a liquid mixture (in this case UDMH) into a large volume space (ullage) above it, the vapor pressure of the resulting liquid mixture decreases. Inversely, as the volume space above the liquid mixture decreases, the vapor pressure of the liquid increases. A preliminary experiment was conducted at Bell to determine the effect this would have when the vapor pressure of the fuel blend was measured at different ullages employing an all-glass evacuated system and an isoteniscope. At 80°F, the vapor pressure at 20% ullage was 3.7 psia, at 50% ullage 3.3 psia, and at 75% ullage 2.3 psia. Although the fuel blend used was slightly out of specification, the effect of ullage was demonstrated.

Table 2.3 and Figure 2.4 contain the vapor pressure of the 50/50 fuel blend at various temperatures and at 46% ullage. The Bell experimental points were obtained with the apparatus shown and described in Reference 2.

TABLE 2.3

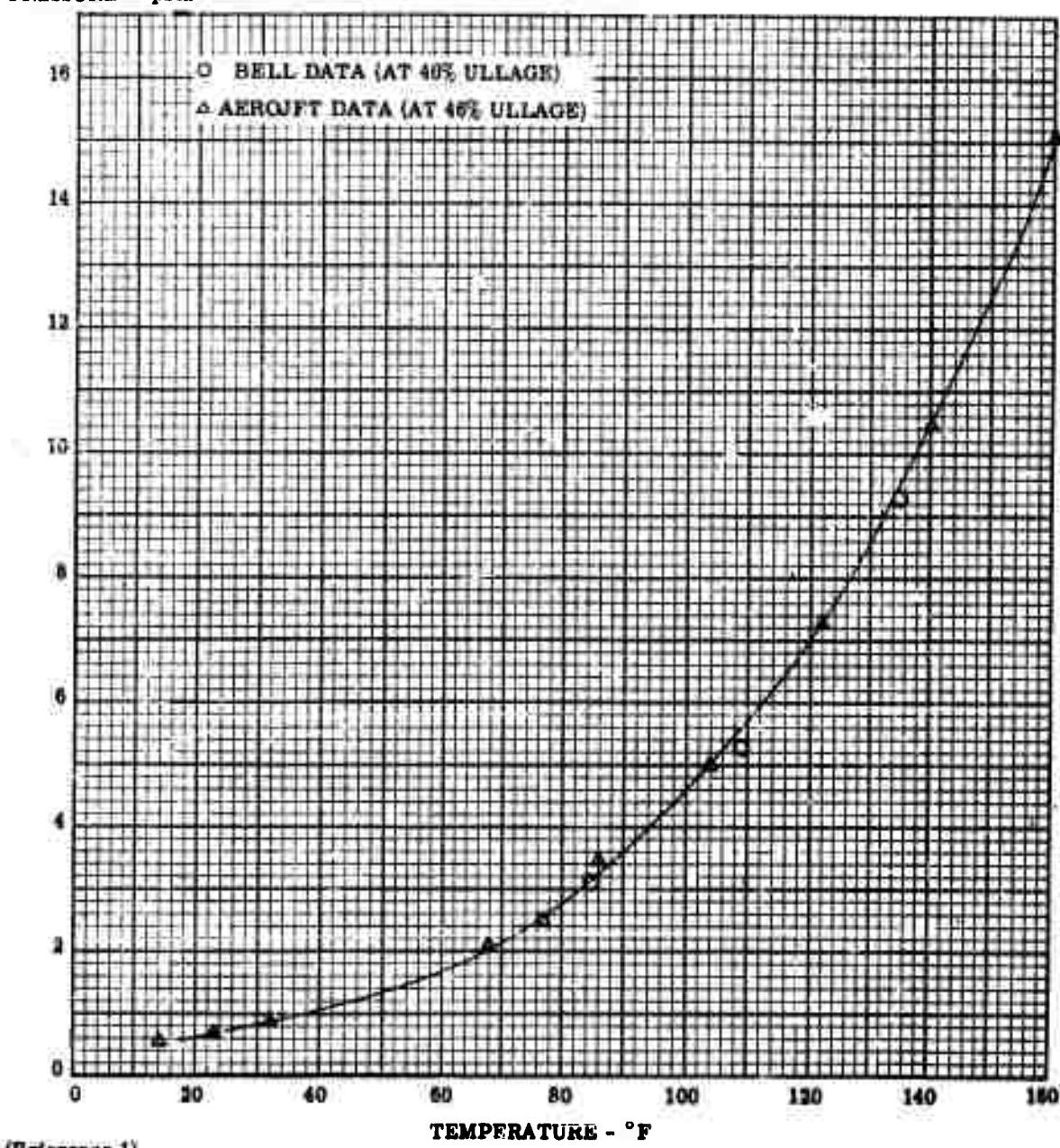
VAPOR PRESSURE OF 50/50 FUEL BLEND AT 46% ULLAGE

Temperature (°F)	Vapor Pressure (psia)
14.0 a	0.55
23.0 a	0.71
32.0 a	0.92
68.0 a	2.09
77.0 a	2.75
85.3 b	3.08
86.0 a	3.42
104.0 a	5.00
108.9 b	5.30
122.0 a	7.30
135.3 b	9.29
140.0 a	10.50
159.8 a	15.10

a - Aerojet-General Corporation experimental data (Reference 1).

b - Bell Aerosystems Company experimental data (Reference 2).

PRESSURE - psia



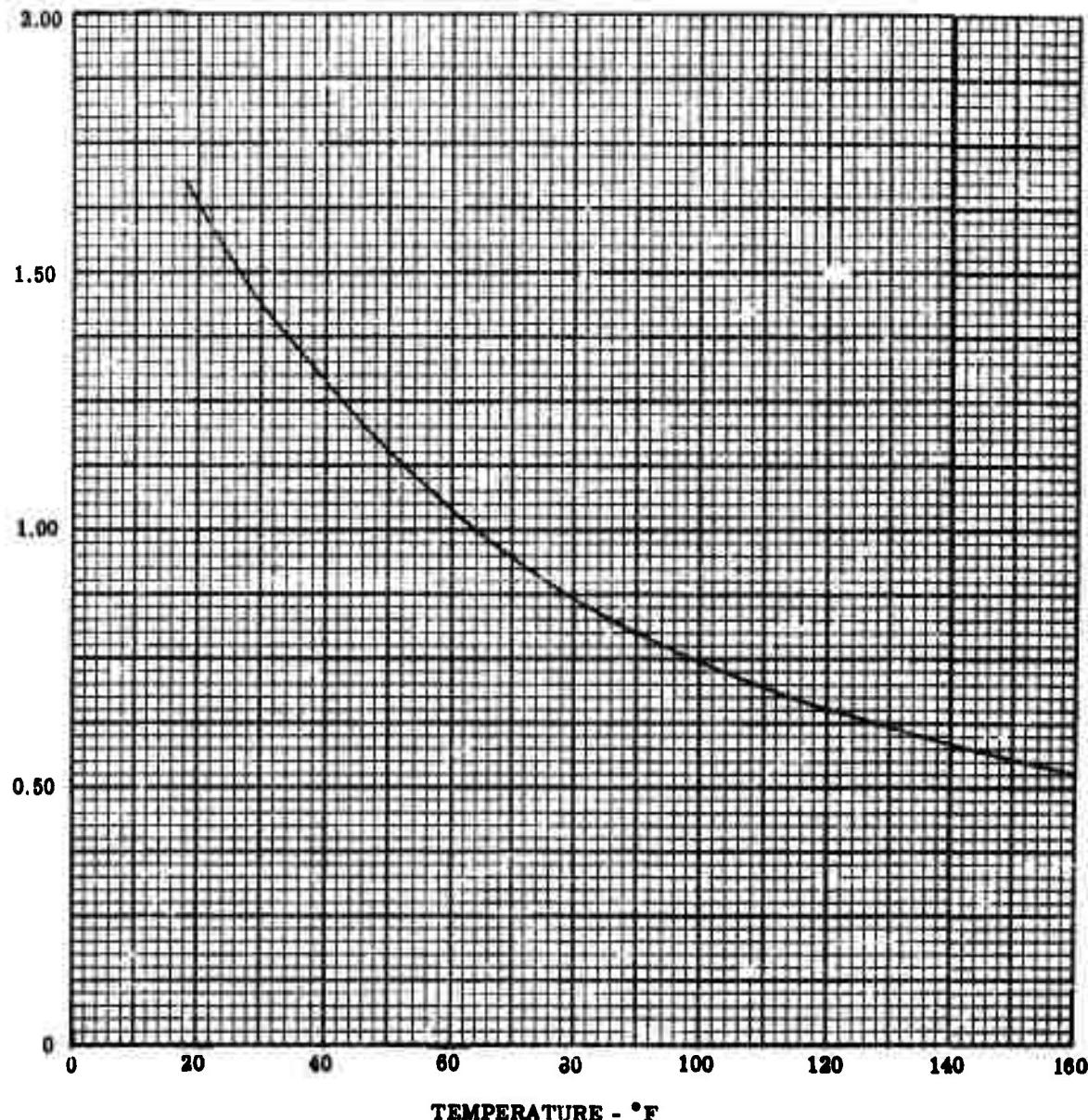
(Reference 1)

Figure 2.4. Vapor Pressure of 50/50 Fuel Blend

2.5 VISCOSITY

The viscosity of the 50/50 fuel blend was measured by Aerojet-General Corporation over the liquid range (Reference 1). Figure 2.5 is a plot of viscosity in centistokes versus temperature of the fuel blend.

VISCOSITY = centistoke



(Reference 1)

Figure 2.5. Viscosity of 50/50 Fuel Blend

2.6 HEAT CAPACITY

Heat capacity data of the 50/50 fuel blend, as calculated by Aerojet-General Corporation, is presented in Table 2.4 and plotted in Figure 2.6. Bell measured the heat capacity of the fuel blend at two temperatures using the method of mixtures described in Reference 2. The Bell experimental data agrees within 0.5% of the Aerojet calculated data.

TABLE 2.4
HEAT CAPACITY OF 50/50 FUEL BLEND
(Calculated by Aerojet-General)

<u>Temperature (°F)</u>	<u>Heat Capacity (BTU/lb- °F)</u>
21	0.680
35	0.684
63	0.692
81	0.696
99	0.702
135	0.709
153	0.715
250	0.743
350	0.780
420	0.814

HEAT CAPACITY - BTU/lb - °F

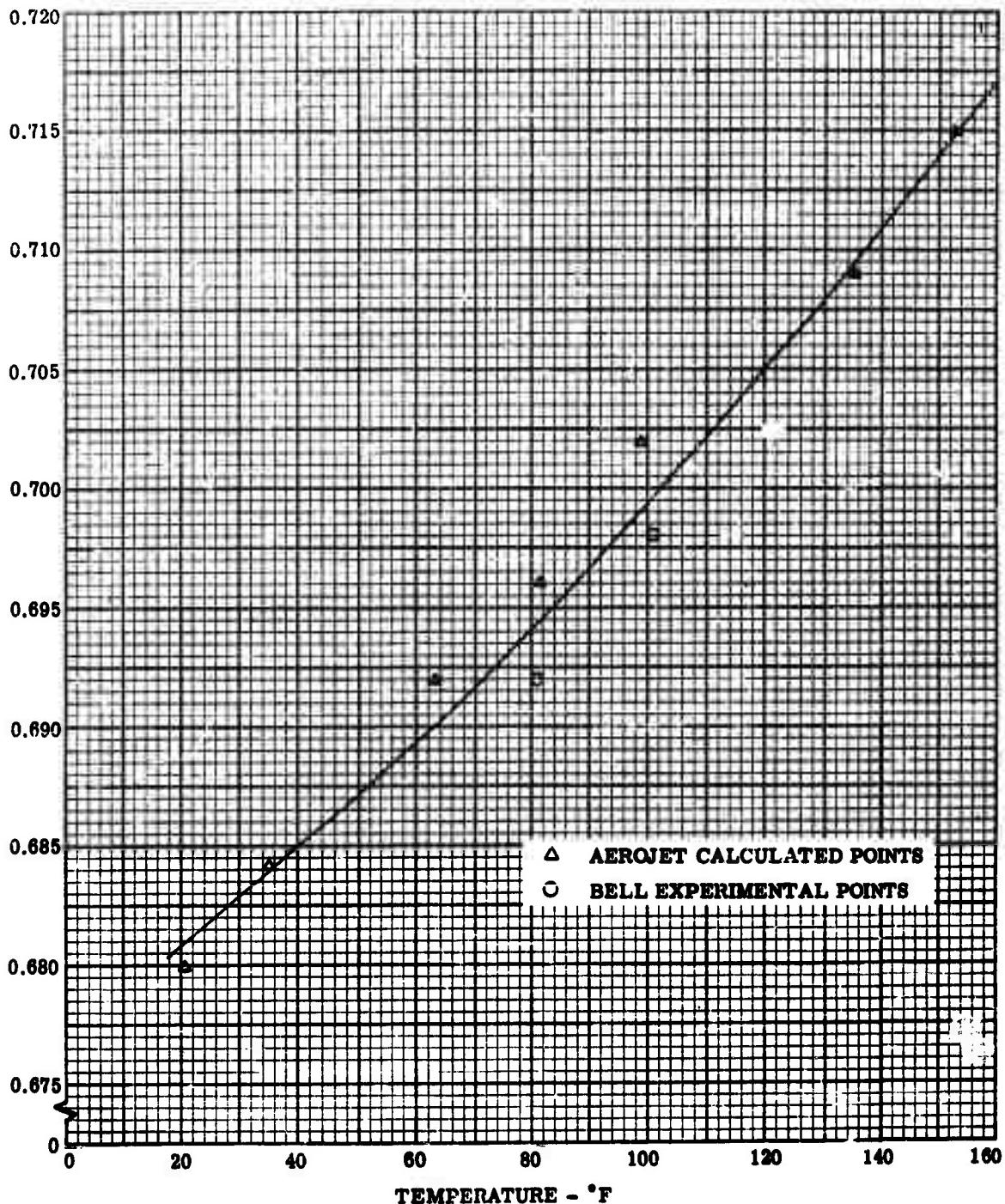


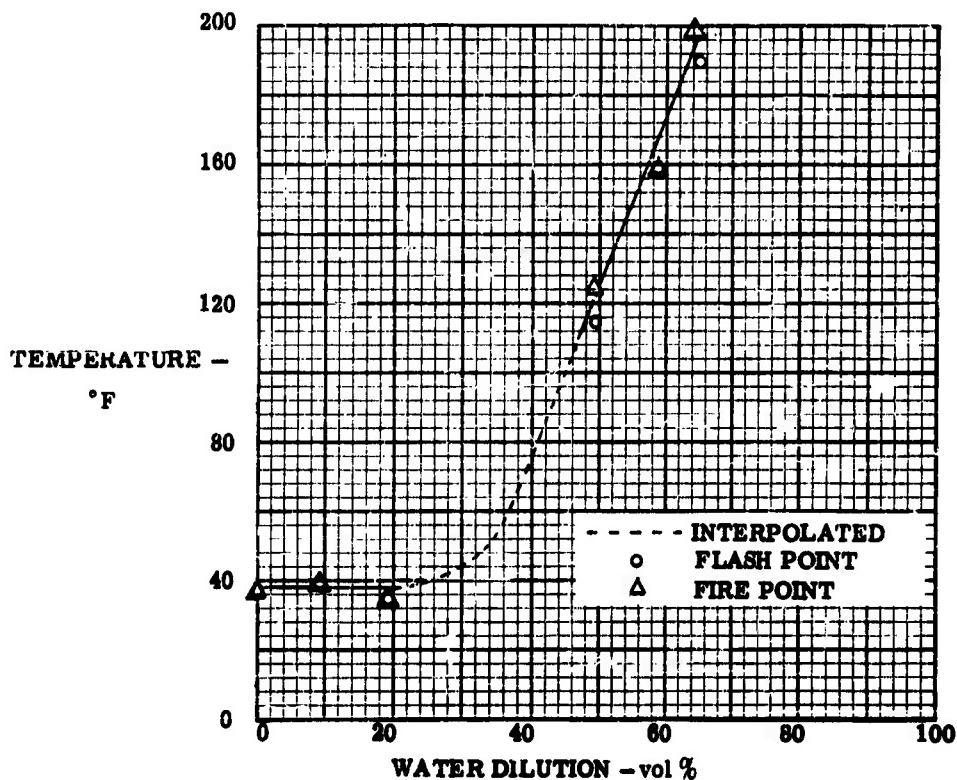
Figure 2.6. Heat Capacity of 50/50 Fuel Blend

2.7 FLASH AND FIRE POINTS

Flash and fire point measurements made with a modified Cleveland Open-Cup Tester (Reference 2) resulted in the data presented in Table 2.5 and plotted in Figure 2.7. The tests indicate that the fuel blend must be diluted with at least an equal volume of water before the fire hazard is reduced appreciably. A dilution of three volumes of water to two volumes of fuel blend is required to increase the flash and fire point temperature to 160° F.

TABLE 2.5
FLASH AND FIRE POINTS OF 50/50 FUEL BLEND
WITH VARIOUS WATER DILUTIONS
(Using a Modified Cleveland Open-Cup Tester)

H ₂ O in Fuel Blend (vol %)	Flash Point (°F)	Fire Point (°F)
Undiluted	38	38
10	40	40
20	35	35
50	110	125
60	160	160
65	180	200
75	> 212	> 212



(Reference 2)

Figure 2.7. Flash and Fire Points of 50/50 Fuel Blend with Various Water Dilutions

2.8 DISTILLATION RANGE

The distillation range of the 50/50 fuel blend, together with analyses of various fractions, is shown in Table 2.6. When the fuel blend is heated, the initial condensed vapors are richer in the more-volatile UDMH; as the distillation process continues with increasing temperature, the condensed distillate becomes richer in the less-volatile N_2H_4 .

TABLE 2.6
DISTILLATION RANGE OF THE 50/50 FUEL BLEND

<u>Blend Composition by Weight %</u>		
UDMH	48.7	
N_2H_4	50.4	
$H_2O + \text{impurities}$	0.9	
149.0	First Drop Distilled	-
158.0	10	86.0% UDMH, 8.0% N_2H_4
161.6	20	85.0% UDMH, 9.0% N_2H_4
167.0	30	-
170.6	40	-
194.0	50	79.0% UDMH, 16.0% N_2H_4
233.6	60	-
235.4	70	-
235.4	80	100% N_2H_4
239.0	90	95% N_2H_4

NOTE: Fuel fractions were analyzed spectrally employing calibration curves covering the UDMH and N_2H_4 concentration range of 45% to 55% by weight. The analytical results, obtained by extrapolating the calibration curves, are approximate. N_2H_4 at the 90% fraction probably contains hydrazine hydrate.

(Reference 2)

2.9 SOLUBILITY OF PRESSURIZING GASES

The solubility of nitrogen, helium, and ammonia in the 50/50 fuel blend was determined using the apparatus shown in Reference 2 and the procedure described in Reference 3. Results of these tests are shown in Table 2.7.

TABLE 2.7
SOLUBILITY OF VARIOUS GASES IN 50/50 FUEL BLEND

Pressurizing Gas	Temperature (°F)	Solubility (wt %)	Final Gas Pressure (psia)
Nitrogen	70.0	< 0.01	86.0
	32.0	< 0.01	79.4
Helium	71.5	0.012 ± 0.008	63.6
	33.0	< 0.008	60.7
Ammonia	57.5	0.26 ± 0.01	38.0
	70.0	0.25 ± 0.01	44.4

2.10 SHOCK SENSITIVITY

To determine the shock sensitivity of the 50/50 fuel blend, tests were conducted at room temperature using a drop-weight tester and a procedure developed by Olin Mathieson Chemical Corporation. The procedure is acceptable to the Joint Army-Navy-Air Force Panel on Liquid Propellant Test Methods. Results of these tests show that the liquid fuel blend is not shock sensitive at the highest impact value (8 foot-pounds) produced by the tester (Reference 2).

AFFTC TR-61-32

2-16

SECTION 3.0

PHYSICAL PROPERTIES OF N₂O₄

SECTION 3.0

PHYSICAL PROPERTIES OF N_2O_4

The compound N_2O_4 is an equilibrium mixture of nitrogen tetroxide and nitrogen dioxide ($N_2O_4 \rightleftharpoons 2NO_2$). At 68°F and at a pressure of one atmosphere, the liquid consists of 84.2% N_2O_4 in equilibrium with 15.8% NO_2 as shown in Table 3.1 and Figure 3.1.

In the solid state, N_2O_4 is colorless; in the liquid state, the equilibrium mixture is yellow to red-brown; and in the gaseous state, it is red-brown. The fumes exhibit a characteristic pungent and irritating odor.

The oxidizer, N_2O_4 , reacts with water forming nitric acid and nitrous acid. The nitrous acid undergoes decomposition immediately forming additional nitric acid and evolving nitric oxide (Reference 30). This strong oxidizer is hypergolic with fuels such as UDMH, N_2H_4 , and aniline.

This section of the handbook contains physical property data for N_2O_4 . The information was obtained from a literature survey. Table 3.2 summarizes the pertinent physical properties of N_2O_4 .

TABLE 3.1
EQUILIBRIUM VALUES - PERCENT DISSOCIATION OF N_2O_4
 $N_2O_4 \rightleftharpoons 2NO_2$

Temperature (°F)	Pressure (psia)		
	<u>7.4</u>	<u>14.7</u>	<u>29.4</u>
68	19.5	15.8	7.2
104	38.7	31.0	15.1
140	66.0	50.4	28.2
176	85.0	73.8	46.7
212	93.7	88.0	66.5

(Reference 5)

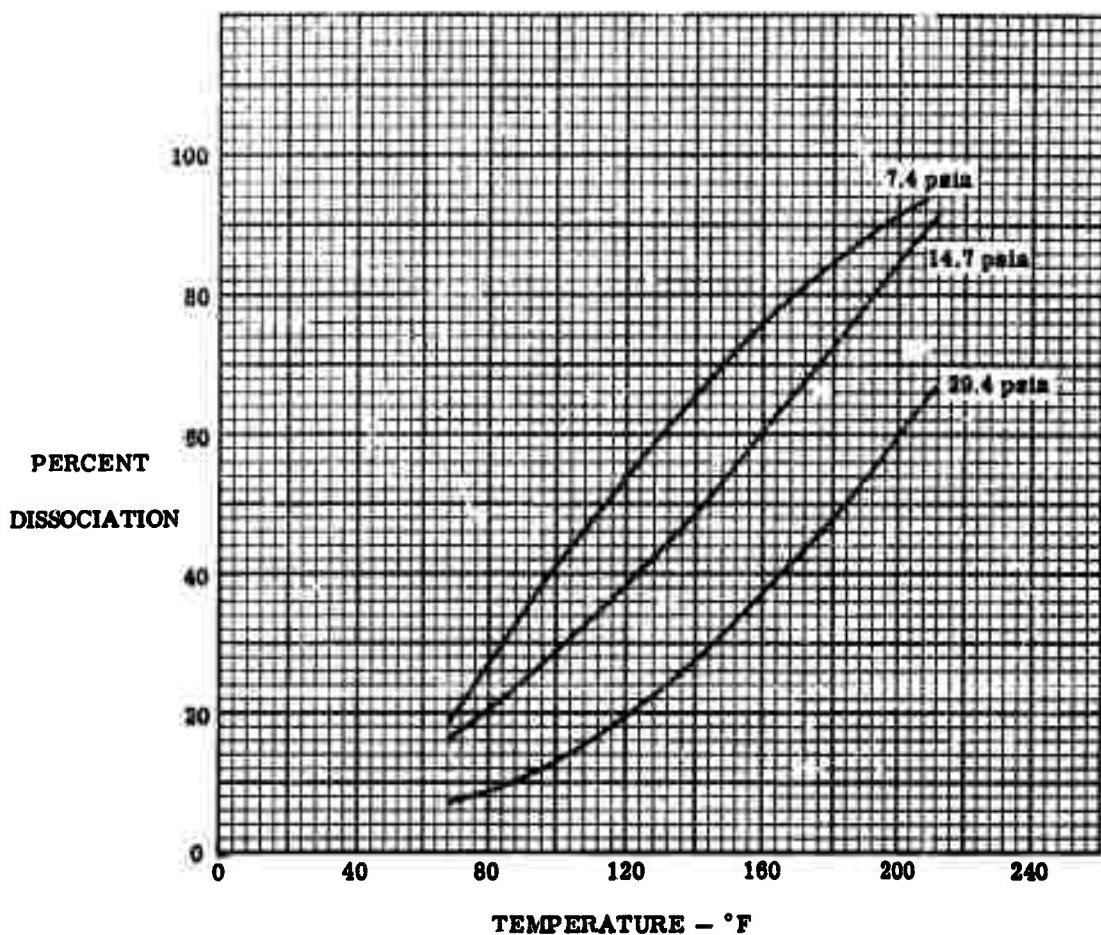


Figure 3.1. Equilibrium Values — Dissociation of N_2O_4

TABLE 3.2
PHYSICAL PROPERTIES OF N₂O₄

	<u>Reference</u>
Empirical Formula	N ₂ O ₄ ⇌ 2NO ₂
Structural Formula	$\begin{array}{c} \text{O} & & \text{O} \\ & \diagdown \quad \diagup \\ & \text{N} - \text{N} \\ & \diagup \quad \diagdown \\ \text{O} & & \text{O} \end{array}$
Molecular Weight	92.016
Physical State	Red-brown liquid
Melting Point	11.84°F
Boiling Point	70.07°F
Heat Formation at 77°F (Liquid)	-87.62 BTU/lb
Vapor Pressure at 77°F	17.7 psia
Viscosity at 77°F	0.0002796 lb/ft-sec 0.410 centipoise
Density at 77°F	89.34 lb/ft ³
Heat Capacity at 70°F	0.370 BTU/lb-°F
Critical Temperature	316.8°F
Critical Pressure	1469 psia
Thermal Conductivity at 40°F and 200 psia	0.0812 BTU/ft-hr-°F
Heat Vaporization	178 BTU/lb
Heat of Fusion	68.4 BTU/lb

3.1 N₂O₄ SPECIFICATION

The chemical requirements for procuring N₂O₄ were taken from Specification MIL-P-26539 (USAF) dated 18 July 1960. These requirements are presented in Table 3.3. The specification contains procedures for performing propellant analysis. The N₂O₄ assay is determined directly by titration. The water content is determined directly by evaporating N₂O₄ and weighing the nitric acid remaining. The water equivalent in this acidic non-volatile matter is based upon the assumption that it is 70% nitric acid. Nitrosyl chloride (NOCl) content is determined by colorimetric means. The non-volatile ash is determined by evaporating N₂O₄ to dryness and igniting the residue at high temperatures. The percentage of non-volatile ash is calculated from the ash that remains.

TABLE 3.3
PROPELLANT SPECIFICATION — N₂O₄

Chemical Requirements	Specification (wt %)
N₂O₄ Assay	99.5 (min)
H₂O Equivalent	0.1 (max)
Chloride as NOCl	0.06 (max)
Non-Volatile Ash	0.01 (max)

3.2 VAPOR PRESSURE

Vapor pressure data, as a function of temperature, is presented in Table 3.4 and plotted in Figure 3.2.

TABLE 3.4
VAPOR PRESSURE OF N₂O₄

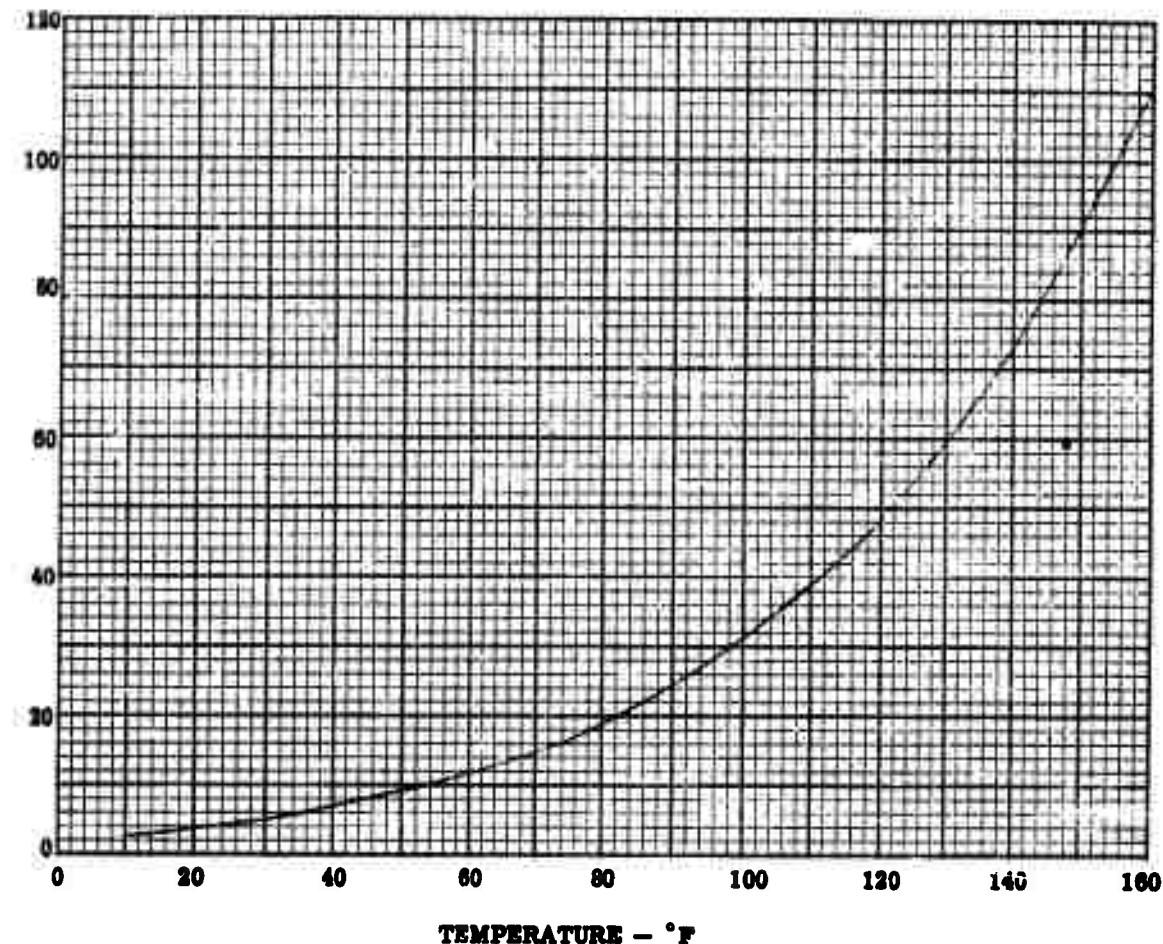
Temperature (°F)	Vapor Pressure (psia)	Temperature (°F)	Vapor Pressure (psia)
11.8	2.70	180	163.29
14	2.90	190	196.35
32	5.08	200	235.01
50	8.56	210	281.56
68	13.92	220	332.8
70	14.78	230	393.2
80	18.98	240	483.3
90	24.21	250	543.9
100	30.69	260	636.3
110	38.62	270	732.6
120	48.24	280	864.1
130	59.98	290	1000.5
140	74.12	300	1160.1
150	91.06	310	1336.5 ^a
160	111.24	316.8 ^b	1469.0 ^a
170	135.14		

a - Value extrapolated.

b - Critical pressure estimated from measured critical temperature.

(References 1 and 5)

PRESSURE - psia



(References 1 and 5)

Figure 3.2. Vapor Pressure of N_2O_4

3.3 DENSITY

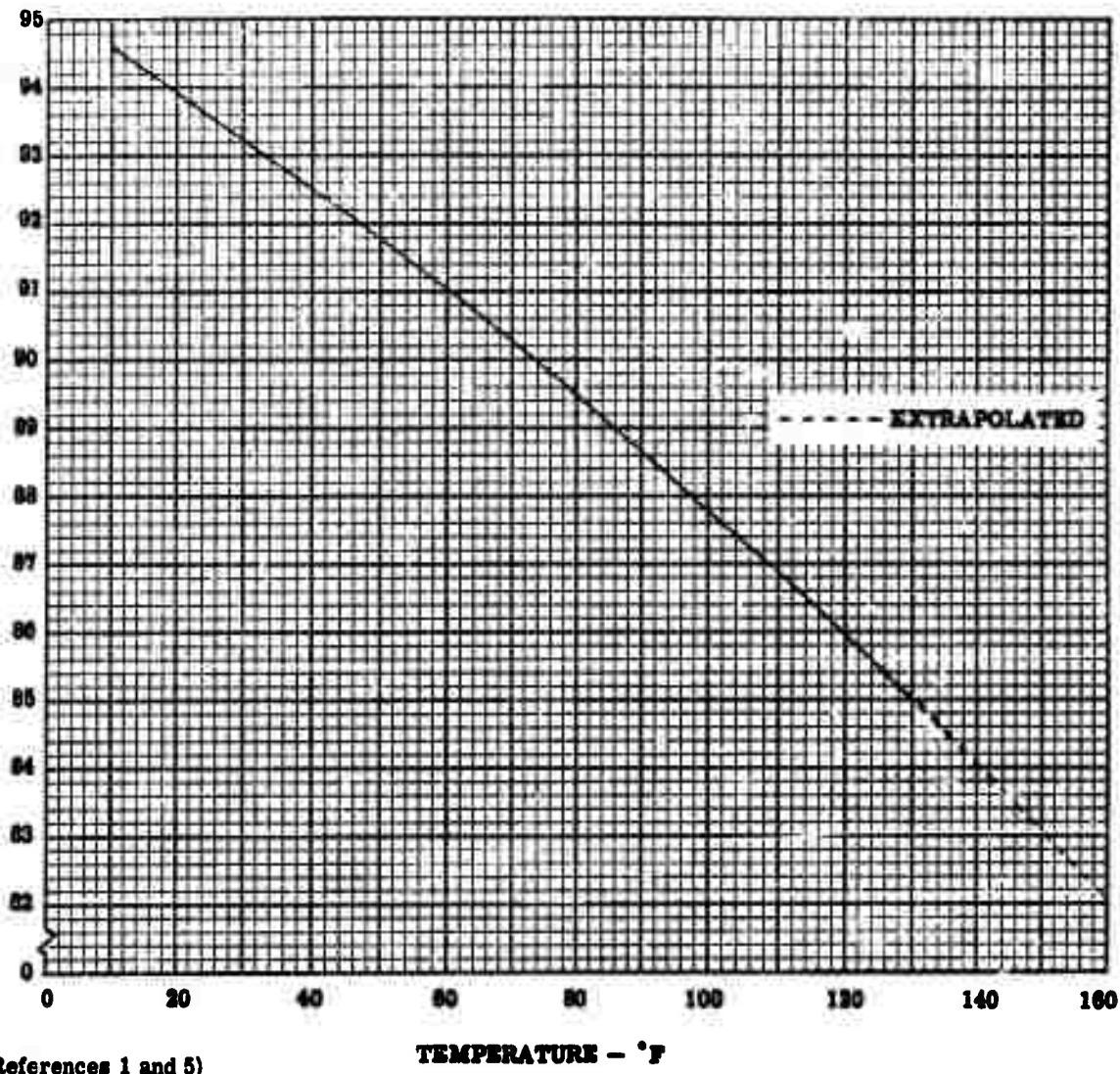
Table 3.5 and Figures 3.3 and 3.4 contain density and specific gravity values as a function of temperature for N₂O₄.

TABLE 3.5
DENSITY OF LIQUID N₂O₄
(Under its Own Vapor Pressure)

Temperature (°F)	Specific Gravity	Density	
		(lb/ft ³)	(lb/gal)
11.8	1.315	94.54	12.62
32.0	1.400	93.05	12.44
50.0	1.470	91.77	12.27
68.0	1.447	90.34	12.09
77.0	1.431	89.34	11.94
95.0	1.412	88.15	11.76
104.0	1.400	87.40	11.66
113.0	1.388	86.61	11.56
118.4	1.379	86.06	11.49
122.0	1.375	85.80	11.45
129.2	1.363	85.06	11.35

(References 1 and 5)

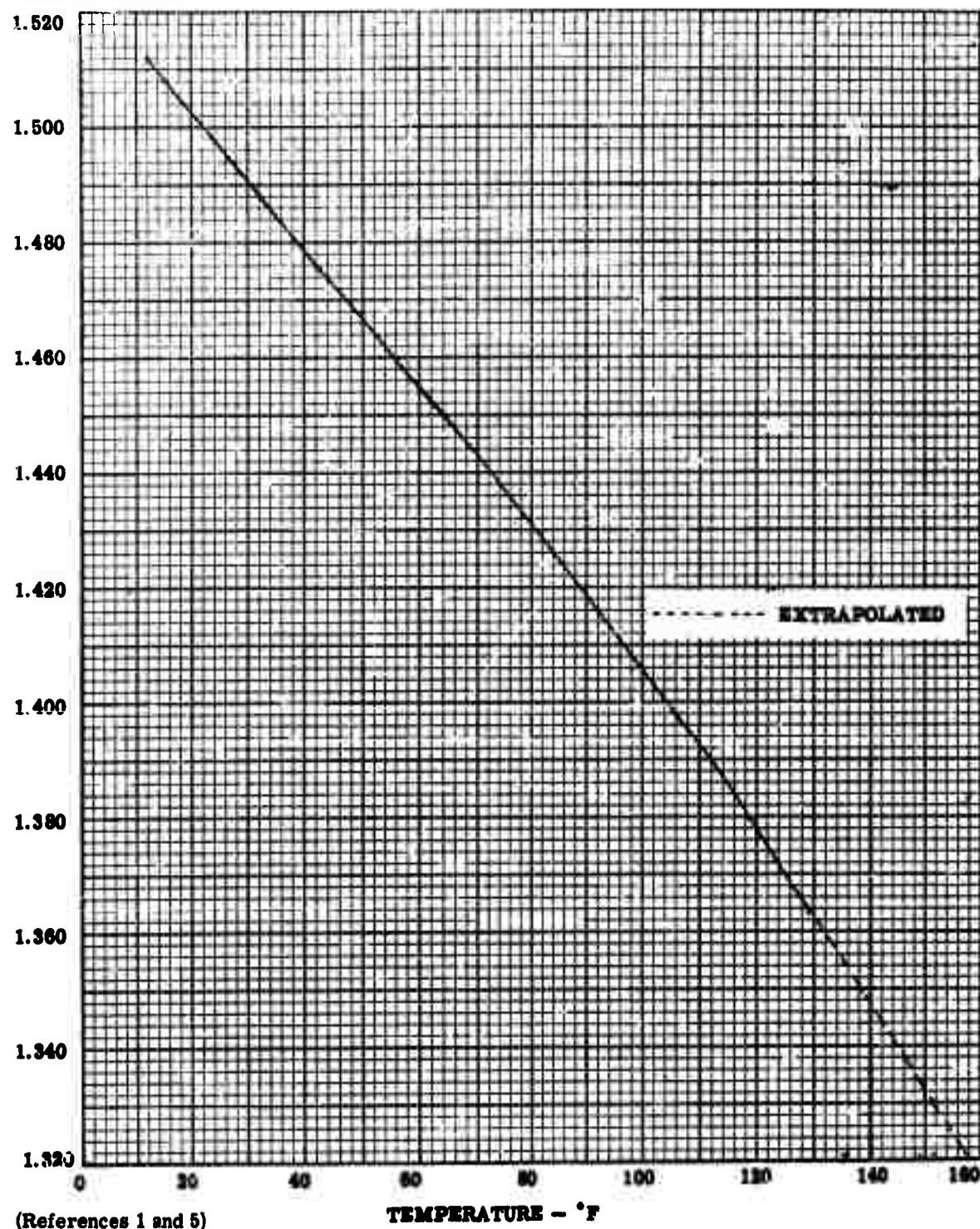
DENSITY — lb/cu ft



(References 1 and 5)

Figure 3.3. Density of N_2O_4 Under its Own Vapor Pressure

SPECIFIC GRAVITY



(References 1 and 5)

TEMPERATURE - °F

Figure 3.4. Specific Gravity of N_2O_4 Under its Own Vapor Pressure

3.4 VISCOSITY

The viscosity of N₂O₄ in the liquid phase from 40° to 280°F is presented in Table 3.6 and plotted in Figures 3.5 and 3.6. Figure 3.5 shows the effect of temperature on the viscosity of N₂O₄; Figure 3.6 shows the effect of pressure on viscosity of N₂O₄.

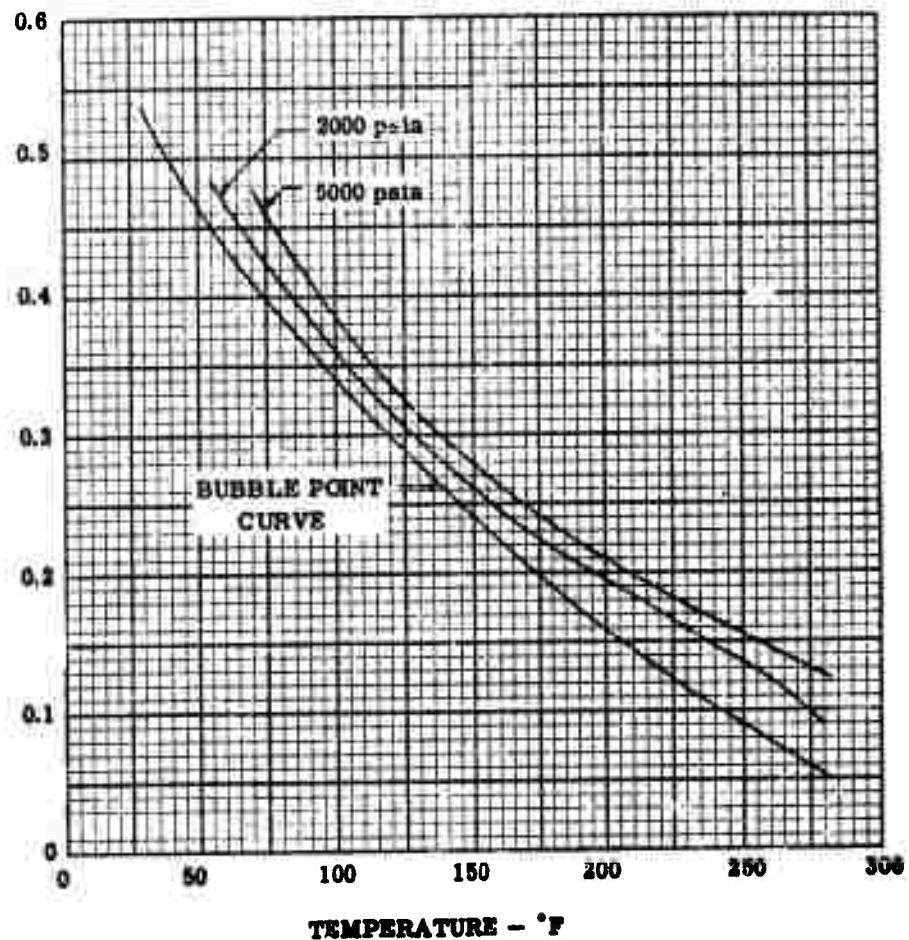
TABLE 3.6
VISCOSITY OF N₂O₄ IN THE LIQUID PHASE

Pressure (psia)	Temperature (°F)								
	40	70	100	130	160	190	220	250	280
	Bubble Pressure (psia)								
	14.8	30.7		60.0	111.2	196.4	332.8	543.9	864.1
Bubble Point	0.4990	0.4132	0.3420	0.2784	0.2235	0.1752	0.1325	0.0924	0.0570
200	0.5021	0.4155	0.3441	0.2800	0.2250	0.1753			
400	0.5055	0.4180	0.3470	0.2820	0.2281	0.1804	0.1350		
600	0.5090	0.4208	0.3495	0.2840	0.2310	0.1850	0.1420	0.0948	
800	0.5121	0.4232	0.3520	0.2861	0.2334	0.1896	0.1482	0.1028	
1000	0.5150	0.4260	0.3544	0.2880	0.2355	0.1939	0.1539	0.1100	0.0630
1250	0.5190	0.4297	0.3566	0.2906	0.2380	0.1975	0.1599	0.1179	0.0713
1500	0.5230	0.4330	0.3587	0.2919	0.2400	0.2010	0.1646	0.1252	0.0798
1750	0.5270	0.4366	0.3608	0.2949	0.2420	0.2040	0.1686	0.1319	0.0881
2000	0.5310	0.4400	0.3628	0.2965	0.2440	0.2083	0.1720	0.1370	0.0940
2200	0.5345	0.4433	0.3649	0.2990	0.2459	0.2060	0.1742	0.1400	0.0990
2500	0.5382	0.4470	0.3670	0.3010	0.2480	0.2098	0.1764	0.1430	0.1045
2750	0.5422	0.4502	0.3691	0.3024	0.2496	0.2110	0.1785	0.1444	0.1090
3000	0.5465	0.4535	0.3713	0.3042	0.2510	0.2127	0.1800	0.1470	0.1120
3500		0.4593	0.3753	0.2070	0.2540	0.2151	0.1822	0.1510	0.1170
4000		0.4655	0.3792	0.3095	0.2568	0.2183	0.1850	0.1532	0.1210
4500		0.4714	0.3830	0.3118	0.2600	0.2200	0.1880	0.1555	0.1249
5000		0.4782	0.3869	0.3145	0.2625	0.2229	0.1900	0.1579	0.1280

(Reference 5)

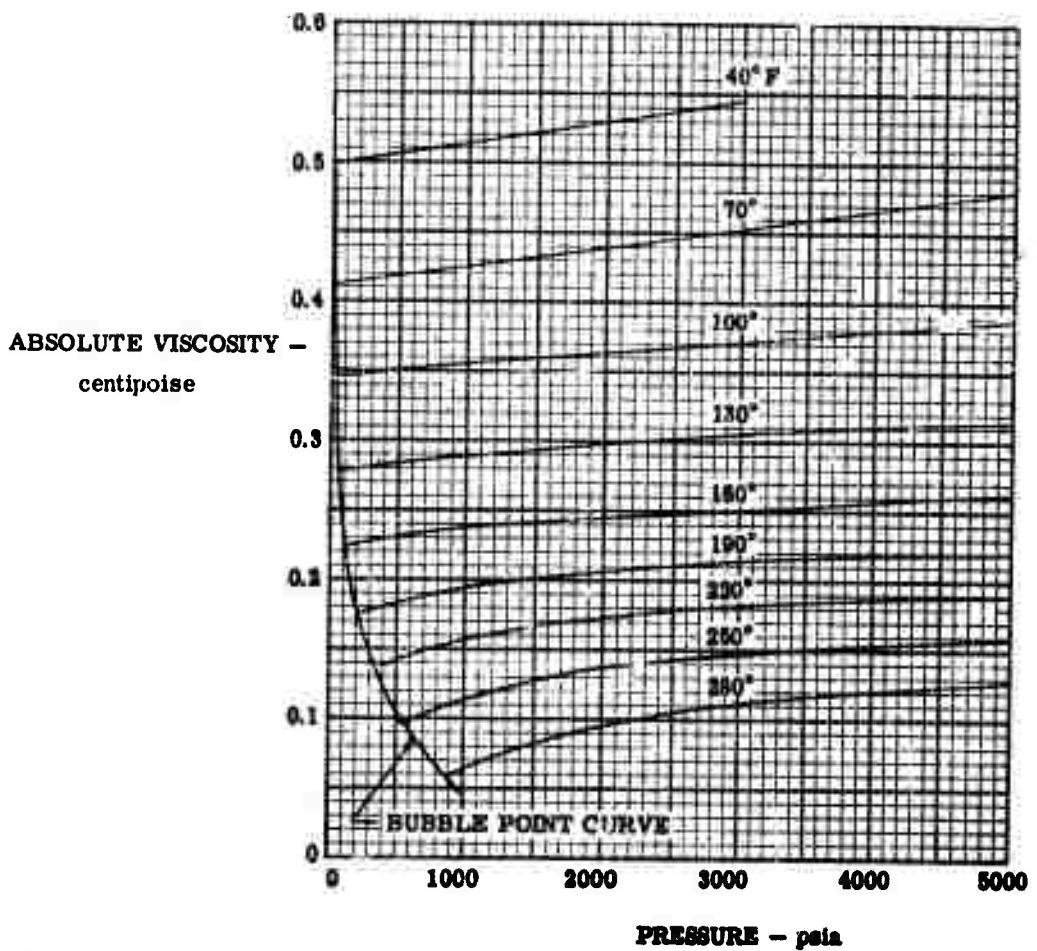
ABSOLUTE VISCOSITY -

centipoise



(Reference 5)

Figure 3.5. Effect of Temperature on Viscosity in the Liquid Phase, N_2O_4



(Reference 5)

Figure 3.6. Effect of Pressure on Viscosity, Liquid N_2O_4

3.5 HEAT CAPACITY

Table 3.7 contains experimental heat capacity data for N_2O_4 . Figure 3.7 is a plot of these points, as well as calculated points obtained by T.F. Morey (Reference 9).

TABLE 3.7
HEAT CAPACITY OF LIQUID N_2O_4

Temperature (°F)	Heat Capacity (BTU/lb-°F)
20.5	0.3564
27.0	0.3578
36.1	0.3598
48.8	0.3624
56.8	0.3652
64.8	0.3667

(Reference 8)

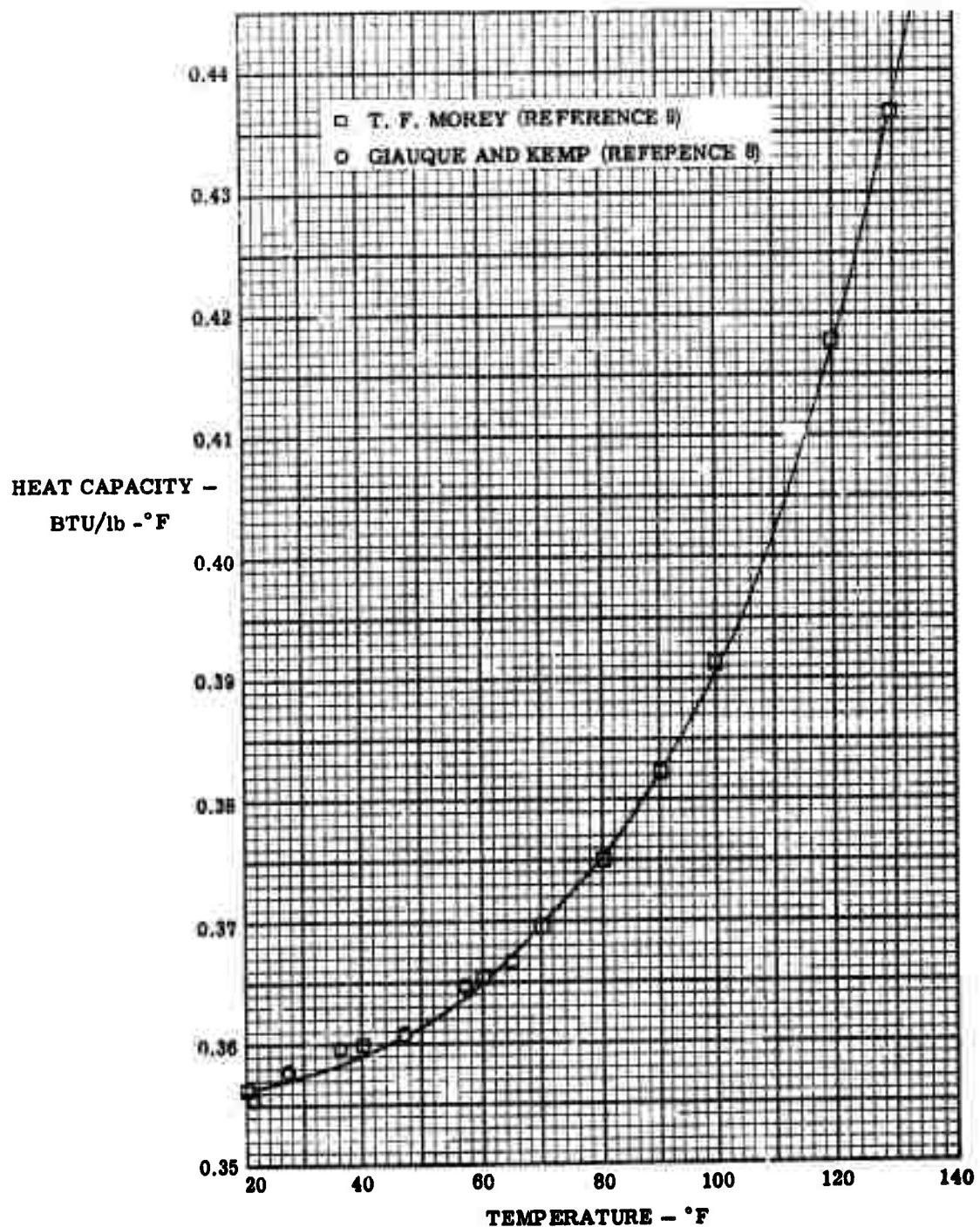


Figure 3.7. Heat Capacity of Liquid N_2O_4

3.6 SOLUBILITY OF PRESSURIZING GASES

The solubility of nitrogen and helium in N_2O_4 was determined using the apparatus shown in Reference 2 and the procedure described in Reference 3. Results of these tests are presented in Table 3.8.

TABLE 3.8
SOLUBILITY OF NITROGEN AND HELIUM
IN LIQUID N_2O_4

Pressurizing Gas	Temperature ($^{\circ}$ F)	Solubility (wt %)	Final Gas Pressure (psia)
Nitrogen	70	0.20 \pm 0.01	63.7
	32	0.14 \pm 0.01	64.2
Helium	73	0.04 \pm 0.01	54.3
	32	0.02 \pm 0.01	55.4

(Reference 4)

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3-16

SECTION 4.0

MATERIALS COMPATIBILITY, 50/50 FUEL BLEND

SECTION 4.0

MATERIALS COMPATIBILITY, 50/50 FUEL BLEND

4.1 EFFECTS OF FUEL BLEND ON METALS

As a result of laboratory tests interpreted on the basis of practical experience, the individual metals have been placed into four ratings similar to those used by the Defense Metals Information Center (Reference 17).

- A: These metals are suitable for unrestricted use with the 50/50 fuel blend. Corrosion rates are less than 1 MPY. Typical uses are storage containers and valves where the propellant is in constant contact.
- B: These metals are for restricted uses with the 50/50 fuel blend, such as transient or limited contact. The corrosion rates are a maximum of 5 MPY. Typical uses are for valves and lines on aerospace ground equipment, for hardware that contacts the propellant intermittently in the liquid and vapor phases, and for pumps and feed lines in which the residence time is limited to loading and unloading.
- C: These metals have limited resistance and corrosion rates between 5 and 50 MPY. Typical use is where the metals are exposed to spillage and momentary contact, such as test stand hardware and aerospace ground equipment. These metals also have application where corrosion can be tolerated to the extent that it will not affect functional operations.
- D: These metals are not recommended for use because their corrosion rates exceed 50 MPY and they cause propellant decomposition.

Table 4.1 contains pertinent compatibility data, references, and ratings for some metals and metal alloys exposed to the 50/50 fuel blend.

4.1.1 Aluminum Alloys

Aluminum alloys are protected from corrosion by naturally occurring oxide films on their surfaces. In certain alkali media like, 50/50 fuel blend, the aluminum alloy is highly resistant to attack. Often, the presence of foreign substances in the medium, rather than the degree of alka-

linity, is the controlling factor in the corrosion of aluminum alloys. The non-sparking tendencies of these alloys are desirable when handling explosive and flammable liquids.

The mechanical properties of the aluminum alloys are not affected by exposure to the 50/50 fuel blend (References 4, 10, and 11). There is no apparent correlation between the alloying constituents of the aluminum alloys and corrosion resistance in this fuel blend.

Welded 2014-T6 was given a "B" rating after exposure to fuel blend containing 3% water. Except for this case, the other aluminum alloys show excellent resistance to the 50/50 fuel blend. Rather than weight loss, most of these alloys experience slight weight gains after fuel exposure. Consideration is to be given to the proper cleaning and surface preparation of aluminum alloys to remove any heterogeneity on the surface resulting from fabrication techniques.

4.1.2 Stainless Steels

The fuel blend is a reducing agent and is slightly alkaline. From the standpoint of corrosion rate, the stainless steels are unaffected. Staining and minor deposits have been found in the vapor phase of 304L, 321, 347, 17-7 PH, 410, and 440C stainless steels which had not been acid-pickled prior to test (Reference 4). Acid-pickling remedies the deposit formation on the 300 series SS but does not for 410SS. Similar deposits are not found on PH 15-7 Mo, AM 355, and 316 stainless steel alloys which did not receive acid-pickling (Reference 4). Apparently, the existence of molybdenum in these alloys affords protection from the formation of deposits.

In general, the use of molybdenum-bearing stainless steel alloys with N₂H₄ are avoided; however, instances are cited in Reference 3 where Rocketdyne, Aerojet, JPL, and Bell Aerosystems have used alloys of this type with N₂H₄ without adverse incident. Testing of these stainless steel alloys with the fuel blend at 160° F for 90 days (Reference 4) resulted in an "A" rating for each alloy. Type 316 stainless steel was given an "A" rating when tested with the fuel blend containing up to 16% water.

4.1.3 Ferrous Alloys

Under ordinary temperatures, both moisture and oxygen are necessary for the corrosion of ferrous alloys in neutral or near-neutral media. Low concentrations of alkali have little to no effect on the corrosion of these alloys. Care should be exercised when using ferrous alloys because of the possible catalytic decomposition of the fuel blend due to rust.

Fuel blend spread on a rusted iron surface in contact with air may generate enough heat to cause spontaneous ignition. Experiments at Aerojet show that the probability of such reactions is low at ordinary ambient temperatures. Drops of fuel blend on heavily rusted surfaces in an air atmosphere at 150° to 160° F did not ignite (Reference 1).

Rust oxidizes N_2H_4 and may be a decomposition catalyst under certain conditions. Aerojet rapidly added a laboratory quantity of N_2H_4 to a few grams of ferric oxide at room temperature without any evidence of gross effects (Reference 1). However, if two to three drops of N_2H_4 are dropped onto a layer of ferric oxide spread on the bottom of a glass flask, ignition occurs in air at room temperature (Reference 44). The N_2H_4 -air interface in the latter case is relatively large and the decomposition due to oxidation by both air and ferric oxide is so rapid that the N_2H_4 quickly ignites. In a nitrogen blanket, ignition did not occur until the nitrogen was replaced by air.

These experiments indicate that the surface area of the rust, the volume of liquid N_2H_4 , and the presence of air are important factors in the rapid decomposition of N_2H_4 . Vapors of N_2H_4 near 235°F are especially susceptible to explosive decomposition and metal oxides such as rust undoubtedly contribute to this reaction.

4.1.4 Nickel Alloys

In general, nickel and nickel alloys are corrosion resistant to the 50/50 fuel blend.

4.1.5 Titanium Alloys

Titanium alloys are resistant to 50/50 fuel blend corrosion. Titanium C120AV has been tested with the 50/50 fuel blend containing as much as 16% water without adverse effects.

4.1.6 Magnesium Alloys

Magnesium alloys show poor resistance to the 50/50 fuel blend.

4.1.7 Cobalt Alloys

Haynes Stellite 25, a cobalt-chrome alloy, exhibits good resistance to the fuel blend.

4.1.8 Copper Alloys

Berylico 25 darkens during exposure to the fuel blend, but exhibits good corrosion resistance. In general, copper alloys are recommended only for limited use with the fuel blend (Reference 15).

4.1.9 Platings

Gold-plated Berylico 25 darkens during exposure to the fuel blend, but exhibits good corrosion resistance. Non-porous chromium and nickel platings are satisfactory; electroless nickel is unsatisfactory for fuel blend service. Cadmium and silver plating are satisfactory for use with the fuel blend.

4.1.10 Conversion Coatings

Sulfuric acid anodize, Hardas (hardcoat) anodize, and iridite are the most resistant conversion coatings used on aluminum alloys. A simple fluoride coating on 2014-T6 aluminum is beneficial after exposure to the fuel blend (Reference 45).

4.1.11 Miscellaneous

Titanium carbide with a nickel binder is resistant to the fuel blend. Microseal 100-1 and 100-1CG graphite-ceramic type coatings on two magnesium alloys do not protect the alloys from corrosion.

TABLE 4.1
COMPATIBILITY OF METALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE									
		LIQUID			VAPOR			INTERFACE			
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	REMARKS
ALUMINUM ALLOYS											
1100	55-60	180	A	15							2% H ₂ O
	55-60	90	A	15							
2014-T6 Sheet											
Unwelded	55-60	180	A ^b	15	180	A ^b	15	180	A	15	Up to 16% H ₂ O, stain at interface and vapor phase
	160	90	A ^b	4	90	A ^b	4	90	A	4	1% H ₂ O added
Welded	55-60	180	A	15	180	A	15				3% H ₂ O added
	55-60	160	B	15							Staining in vapor
	160	14	A	4							"D" rating because of cracks in heat affected zone
Spotwelded	55-60	180	D	15							
2014-T6 Extrusion	160	90	A ^b	4	90	A ^b	4	90	A	4	
Unwelded and stressed to 30,000 psi	55-60	180	A	15							
Welded and stressed to 30,000 psi	55-60	180	A	15							
2024-T6	160	90	A ^b	4	90	A ^b	4	90	A	4	

a -- Definitions of ratings are given on page 4-1.

b -- Predicted rating from interface data.

TABLE 4.1 (CONT)
COMPATIBILITY OF METALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE									
		LIQUID			VAPOR			INTERFACE			
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	REMARKS
ALUMINUM ALLOYS (CONT)											
2219-T61 Welded and Unwelded	55-60	180	A	15							
3003-H14	150							1	A	14	
5086-H36 Unwelded	160	90	A ^b	4	90	A ^b	4	90	A	4	
Welded	160	14	A	4							
5354-F	160	90	A ^b	4	90	A ^b	4	90	A	4	Up to 10% H ₂ O dis-coloration in both phases
5456-H24	55-60	180	A	15							
5456-H321 Unwelded	160	90	A ^b	4	90	A ^b	4	90	A	4	7% H ₂ O
160	14	A	4								
Stressed to 30,000 psi	55-60	90	A	15							7% H ₂ O
Welded	55-60	90	A	15	30	A	10				7% H ₂ O
160	14	A	4								
Stressed to 30,000 psi	55-60	30	A	15							7% H ₂ O
6061-T6											
Unwelded	55-60	180	A	15				0			00
	160	14	A	4							

a - Definitions of ratings are given on page 4-1.

b - Predicted rating from interface data.

TABLE 4.1 (CONT)
COMPATIBILITY OF METALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE						REMARKS	
		LIQUID		VAPOR		INTERFACE			
		TIME IN DAYS	RATING ^a	TIME IN DAYS	RATING ^a	TIME IN DAYS	RATING ^a		
ALUMINUM ALLOYS (CONT)									
6061-T6									
Unwelded	100	90	A ^b	4	90	A ^b	4	Stain in interface, up to 16% H ₂ O	
Welded	55-60	180	A	15				2% H ₂ O	
	55-60	30	A	15					
	100	14	A	4					
6063	100	90	A ^b	4	90	A ^b	4		
T075-T8	55-60	90	A ^b	15	90	A ^b	4	Multicoloration in vapor phase	
	100	90	A ^b	4	90	A ^b	4	2% H ₂ O	
Stressed to 80% yield	55-60	30	A	15					
206	100	90	A ^b	4	90	A ^b	4	Up to 16% H ₂ O, staining in vapor phase	
	55-60	90	A ^b	15					
Tens 50	100	90	A ^b	4	90	A ^b	4	Staining in vapor	
STAINLESS STEEL									
303	100	90	A ^b	4	90	A ^b	4	Stain in vapor	
304L	55-60	180	A	15					
	100	14	A	4					
	100								
Welded	100	14	A	4				Deposits in vapor, up to 16% H ₂ O	

a - Definitions of ratings are given on page 4-1.

b - Predicted rating from interface data.

TABLE 4.1 (CONT)
COMPATIBILITY OF METALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE									
		LIQUID			VAPOR			INTERFACE			
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	REMARKS
STAINLESS STEELS (CONT)											
316	160	90	A ^b	4	90	A ^b	4	90	A	4	Stains in vapor, up to 1-1/2 HgO
321	160	14	A	4				90	B	4	Deposits in vapor
Welded	160	14	A	4							Stains in vapor
	55-60	180	A	15							Stains in vapor
347	160	14	A	4				90	B	4	Deposits in vapor
Welded	55-60	180	A	15	180	A	15	180	A	15	
	160	14	A	4							
PH 15-7 Mo Cond. A	160	90	A ^b	4	90	A ^b	4	90	A	4	Stain in vapor; no deposits
17-4 PH	160	90	A ^b	4	90	A ^b	4	90	A	4	Stain in vapor; no deposits
17-7 PH Cond. A	160							90	B	4	Deposits in vapor
AM 355 Cond. H	160	180	A ^b	4	180	A ^b	4	180	A	4	Stain in vapor; no deposits
410 H & T	160							90	B	4	Deposits in vapor
Welded	160	14	B	4							Deposits in vapor
440 C	160							90	B	4	Deposits in vapor

^a - Definitions of ratings are given on page 4-1.^b - Predicted rating from interface data.

TABLE 4.1 (CONT)
COMPATIBILITY OF METALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE						REMARKS	
		LIQUID		VAPOR		INTERFACE			
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE		
<u>FERROUS ALLOYS</u>									
1020	55-60	180	C	15					
4130	55-60	180	C	15					
A 386	55-60	180	C	15				These would have an "A" rating except for their susceptibility to rusting	
<u>NICKEL ALLOYS</u>									
Nichrome	180	90	A ^b	4	90	A ^b	4		
Nilvar	55-60	180	A	15					
NI Spinel C	55-60	30	A	15				5% HgO	
<u>TITANIUM ALLOYS</u>									
BT130 VCA	55-60	180	A	15					
	180	90	A ^b	4	90	A ^b	4		
Al110-AT	180	90	A ^b	4	90	A ^b	4		
Cl130 AV	55-60	30	A ^b	15				5% HgO	
	180	90	A ^b	4	90	A ^b	4	Up to 10% HgO	
<u>MAGNESIUM ALLOYS</u>									
HM21A-T8	55-60	30	D	15				Pitted	
<u>COBALT ALLOYS</u>									
Haynes Stellite 35	180	90	A ^b	4	90	A ^b	4		

^a - Definitions of ratings are given on page 4-1.^b - Predicted rating from interface data.

TABLE 4.1 (CONT)
COMPATIBILITY OF METALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE											
		LIQUID			VAPOR			INTERFACE			REMARKS		
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE
COPPER ALLOYS													
Berylico 25	160	90	A ^b	4	90	A ^b	4	90	A	4	Darkened		
PLATINGS													
Cadmium	55-60	-	C	15									
Chromium (non-porous)	55-60	-	A	15									
Copper	55-60	-	C	15									
Gold on Berylico 25	160	90	A ^b	4	90	A ^b	4	90	A	4	Darkened		
Nickel Electrolytic (non-porous)	55-60	-	A	15									
Electroless	55-60	-	D	15									
Silver	55-60	-	D	15									
Tin	55-60	-	D	15									
Zinc	55-60	-	D	15									
COATINGS ON ALUMINUM ALLOYS													
Iridite 2014-T6	55-60	180	A	15									
Alodine 2014-T6	160								90	B	4	Lost weight; stain at interface; up to 16% H ₂ O	
6061-T6	160	90	A ^b	4	90	A ^b	4	90	A	4	Gained weight; up to 16% H ₂ O		
Hardas (Hardcoat) Anodize 2014-T6	55-60	180	A	15									

a - Definitions of ratings are given on page 4-1.

b - Predicted rating from interface data.

TABLE 4.1 (CONT)
COMPATIBILITY OF METALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE										REMARKS
		LIQUID			VAPOR			INTERFACE				
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	REFERENCE
COATINGS ON ALUMI- NUM ALLOYS (CONT)												
Sulfuric Acid Anodize 2014-T8	160	90	A ^b	4	90	A ^b	4	90	A	4	Lost weight; up to 16% H ₂ O; no deposit; some stain	
6061-T6	160	90	A ^b	4	90	A ^b	4	90	A	4	Gained weight; up to 16% H ₂ O; stain at interface	
Fluoride 2014-T6	70-80	9	A	45							"A" rating based on visual examination	
MISCELLA- NEOUS												
Titanium Carbide with Nickel Binder	160	90	A ^b	4	90	A ^b	4	90	A	4		
Silver Solder	55-60	180	A	15				90	D	4	Coating porous metal attacked	
Microseal 100-1 coating on AM 100A Magnesium	160							3	D	4	Coating porous, metal attacked	
Microseal 100-1 CG Coating on AZ 31 C Magnesium	160											

a -- Definitions of ratings are given on page 4-1.
 b -- Predicted rating from interface data.

TABLE 4.1 (CONT)
COMPATIBILITY OF METALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE								REMARKS
		LIQUID		VAPOR		INTERFACE				
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE
BRAZING AND SOLDERING										
6061-T6 Al Brazed with T18 Filler	160	14	A	4						
363 SS Soldered with Pure Tin	160	14	A	4						Tin solder darkened
347 Silver Brazed with Easy Flo per QQ-B- 561 Class 4	160	14	A	4						
347 SS Ni- cobrezaed AMS 4775	160	14	A	4						Stain in vapor
METAL COUPLERS										
2014-T6 Al Bolted to 321 SS	55-50	90	A	10	180	A	15	180	A	15
2014-T6 Al Bolted to 6Al + 4V Titanium	55-60	90	A	10						
2014-T6 Al Welded to 6061-T6 Al	160	14	A	4						
6061-T6 Al Ultrasonic Welded to 321 SS	55-60	90	D	15						"D" rating because of visible cracks in area of poor fusion

a - Definitions of ratings are given on page 4-1.

TABLE 4.1 (CONT)
COMPATIBILITY OF METALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE						REMARKS
		TIME IN DAYS RATING ^a REFERENCE						
METAL COUPLES (CONT)								
6061-T6 Al Spotwelded to 2014-T6 Al	55-80	90 D 15						2% H ₂ O, "D" rating because of weld cracks

a - Definitions of ratings are given on page 4-1.

4.2 EFFECTS OF FUEL BLEND ON NONMETALS

Government specifications^a on rubbers and plastic fabricated parts intended for packings and seals show that the physical property effects to be minimized are volume change, durometer change, effect on media, and visual examination in terms of surface appearance. The specifications contain different values for volume change and durometer change. Using the ranges called for in the specifications, the following ratings were derived for the nonmetals:

	A	B	C	D
Volume Change, %	0 to +25	-10 to +25	-10 to +25	<-10 or >+25
Durometer Reading Change	±3	±10	±10	<-10 or >+10
Effect on Propellant	None	None	Slight Change	Severe
Visual Examination	No Change	No Change	Slight Change	Involved, severely blistered or cracked

Definitions for these ratings are as follows:

- A: Satisfactory for service under conditions indicated.
- B: Use with knowledge that it will swell or shrink and/or change in hardness.
- C: Satisfactory for ground support where preventative maintenance can be scheduled. Also good for actual missile service where slight discoloration of propellant and extracted residue is tolerable.
- D: Unsatisfactory for use.

Table 4.2 contains compatibility data, references, and ratings for several nonmetals exposed to the 50/50 fuel blend.

The fuel blend can dissolve, attack, or decompose nonmetals such as plastics, elastomers, lubricants, and coatings. These reactions usually cause degradation or complete destruction of the material. The fuel can extract components from the material or be absorbed by the material, thereby altering the physical properties. The nonmetals investigated embrace a wide variety of

a-Government Specifications:

MIL-R-2765A	Rubber, Synthetic, Oil Resistant (Sheet, Strip, and Molded Shapes).
MIL-R-3065B	Rubber Fabricated Parts.
MIL-R-8791A	Retainer Packing, Hydraulic and Pneumatic, Tetrafluoroethylene.
HH-P-131C	Packing, Metallic and Nonmetallic, Plastic.
HH-P-166A	Packing, Nonmetallic.

chemical and physical structures; as such, methods of fabrication and geometrical factors greatly influence the behavior of the material.

For example, many materials can be used as gaskets or seals where a definite compression set limitation, and in all probability a volume change limitation, is required for sealing. The gasket or seal can be enclosed between two metal surfaces with only a small portion exposed to the fuel. The swelling characteristics of this type exposure are of less importance than the swelling obtained from complete immersion in the fuel where volume change is magnified. Tensile properties play a small role in the application of a material as a gasket. For this reason, use of the nonmetals must be weighed in terms of the physical properties desired.

4.2.1 Plastics

Teflon and Teflon products are chemically resistant to the 50/50 fuel blend.

Nylons 31, 63, and 101 vary in composition and are highly inert to most solvents; however, their resistance to the 50/50 fuel blend is limited to 90 to 120 days at 70° to 80°F (References 1 and 15). At 160°F, the nylons failed within 30 days (Reference 4).

The polyethylenes have fair resistance to solvents and have a limited use temperature range. In the 50/50 fuel blend, they are subject to stress cracking (Reference 1). The irradiated polyethylene is the most resistant. Kel-F 300 shows cracking tendency (Reference 1) after 70 days at 70° to 80°F and darkens and becomes brittle within 30 days at 160°F (Reference 4).

4.2.2 Elastomers

Butyl rubbers are characterized by good resistance to aging and superior properties over natural rubbers. They are compounded to attain desirable properties. Most butyl rubbers exhibit good resistance to the 50/50 fuel blend.

The fluorosilicones characterized by good heat resistance and fair resistance to solvents show poor resistance to the fuel blend. This is also true of the fluororubbers.

4.2.3 Lubricants and Sealants

All lubricants except Microseal 100-1 dissolve or wash out to varying degrees when exposed to the 50/50 fuel blend. The UDMH Lube is the most satisfactory based upon service and dynamic tests performed on an O-ring (Reference 4). Lox Safe, ANDOK-C, and S#58-M oil show promise and could be considered for service. Reddy Lubes 100 and 200 and water glass/graphite blend are satisfactory sealants with the fuel blend.

4.2.4 Potting Compounds and Ceramics

Only Crystal M & CF, a potting compound, is satisfactory for limited use with the fuel blend. Temporell, Sauereisen P-1 and 31, and Rockflux are ceramics satisfactory for service with the fuel blend.

4.2.5 Adhesives

Armstrong A-6 and HT 424 are adhesives reported satisfactory for service with the fuel blend.

4.2.6 Paints

Tests to date indicate that no paints are compatible with the fuel blend.

TABLE 4.2
COMPATIBILITY OF NONMETALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE					
		LIQUID		VAPOR		TIME IN DAY ^a	RATING ^a
		TIME IN DAY ^a	RATING ^a	REFERENCE	TIME IN DAY ^a	RATING ^a	REFERENCE
PLASTICS							
Polytetra-fluoroethyl-ene							
Teflon (TFE)	55-60	180	A	15			Up to 5% H ₂ O
	70-80	120	A	1			
	100	30	B	4			Shrinks 4.5%, 7% tensile loss
	120	15	C	15			5% H ₂ O
Teflon filled with graphite	55-60	180	A	15			
Teflon filled with molydisulfide	55-60	180	A	15			5% H ₂ O
Teflon filled with asbestos	55-60	90	A	15			5% H ₂ O
Armalon 7700 im-pregnated with Teflon fibers	55-60	90	C	15			5% H ₂ O, fuel discolored
Armalon 7700B im-pregnated with Teflon fibers	55-60	90	A	15			5% H ₂ O
Fluorobes-tos filled with asbestos	55-60	90	A	15			5% H ₂ O
TFE-felt 7550	55-60	90	C	15			5% H ₂ O, fuel discolored

^a -- Definitions of ratings are given on page 4-14.

TABLE 4.2 (CONT)
COMPATIBILITY OF NONMETALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE		STATIC EXPOSURE			REMARKS
	DEGREES FAHRENHEIT		LIQUID		VAPOR	
	TIME IN DAYS	RATING*	REFERENCE	TIME IN DAYS	RATING*	REFERENCE
PLASTICS (CONT)						
Fluorinated Propylene Co-polymer						
Teflon (FEP)	55-60	180	A	15		Up to 3% H ₂ O
	70-80	60	A	1		
	160	30	B	4		Shrinks 15.8%
Polychloro-trifluoro-ethylene						
Kel-F 300 Unplasticized	55-60	180	A	15		Up to 3% H ₂ O
	70-80	70	B	1		Hardened, cracking tendency
	160	30	D	4		Blackened, became fragile
Kel-F Annealed	55-60	90	A	15		2% H ₂ O
Polyethylene						
Low Density	55-60	30	A	11		
Hi Density	160	30	C	4		Shrinks 10.8%
Marlex 50 Hi Density	55-60	90	B	15		2% H ₂ O, shrinks 2.2%
Polyolefin						
White insulation	160	30	A	4		
Black insulation	160	30	C	4		Fuel discolored

* -- Definitions of ratings are given on page 4-14.

TABLE 4.2 (CONT)
COMPATIBILITY OF NONMETALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE					
		TIME IN DAYS		REFERENCE	TIME IN DAYS		REFERENCE
		LIQUID	VAPOR		LIQUID	VAPOR	
PLASTICS (CONT)							
Polypropylene							
From Hercules	55-60	90	A	10			
From Chicago Molded Products	180	30	A	4			5.1% tensile loss
Polyamide-Nylon							
Zytel 31	70-80	110	A	1			
	160	7	D	4			Crumpled
Zytel 63	70-80	-	D	1			Dissolved
Zytel 101	55-60	180	D	15			1% H ₂ O, disintegrating
	70-80	120	B	1			Softened 1%
	160	7	D	4			Crumpled
Polyester							
Mylar	55-60	30	D	11			Dissolved
Laminates-Glass							
Silicone (composition unknown)	55-60	180	C	15			Partially delaminated
Phenolic (composition unknown)	55-60	180	C	15			Fuel discolored, partially delaminated
Epoxy (composition unknown)	55-60	180	D	15			Delaminated

a - Definitions of ratings are given on page 4-14.

TABLE 4.2 (CONT)
COMPATIBILITY OF NONMETALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE				REMARKS	
		LIQUID		VAPOR			
		TIME IN DAY RATING ^a	REFERENCE	TIME IN DAY RATING ^a	REFERENCE		
PLASTICS (CONT)							
Polyester (composition unknown)	55-60	30	D	11		Delaminated	
Polyvinylidene Chloride							
Saran	55-60	30	D	15			
Polyformaldehyde							
Delrin	55-60	90	D	10		Shrinks 3%, increased in hardness 2%	
Polycarbonate							
Lexan	55-60	30	D	11		Dissolved	
Polyvinyl Fluoride							
Teslar	55-60	30	B	11		Shrinks 4.4%	
Polymethyl Methacrylate							
Plexiglass	55-60	90	D	15		Cracking and dissolving	
UTYL RUBBERS							
Perco 823-T0	70-80	143	B	1		Softened 20%	
Preciation Number 9257, 9357	70-80	50	B	1		Softened 13%	

^a - Definitions of ratings are given on page 4-14.

TABLE 4.2 (CONT)
COMPATIBILITY OF NONMETALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE					
		TIME IN DAYS		RATING ^a	REFERENCE	TIME IN DAYS	
		LIQUID	VAPOR			RATING ^a	REFERENCE
BUTYL RUBBERS (CONT)							
Parker B480-7	70-80	162	D	1			Softened 20%
Parco 805-70	70-80	68	D	1			Softened 37%, fuel discolored amber
	160	30	C	4			Precipitate extracted, tensile loss 28.8%
Coshen 1357	70-80	68	D	1			Softened 12%, fuel discolored amber
	160	30	C	4			Precipitate extracted, tensile loss 28.5%
Enjay 268	55-80	30	C	15			Fuel discolored yellow
Enjay 551	55-80	30	C	15			Fuel discolored yellow
Precision 214-907-9	160	1	D	4			Violent reaction - compound similar to Enjay 62790
	70-80	7	-	4			No violent reaction
Hycar 2202	55-80	30	D	11			43%, fuel yellow
Linear 7806-70	160	30	D	4			Precipitate extracted, cracked
Parker XB800-71	160	30	A	4			Tensile loss 6.6%
Parker B496-7	160	30	A	4			Tensile loss 11.4%
Parker 318-70	160	30	C	4			Precipitate extracted, tensile loss 20.7%

a — Definitions of ratings are given on page 4-14.

TABLE 4.2 (CONT)
COMPATIBILITY OF NONMETALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE				REMARKS
		TIME IN DAYS RATING ^a REFERENCE	TIME IN DAYS RATING ^a REFERENCE	LIQUID	VAPOR	
BUTYL RUBBERS (CONT)						
Stillman 613-75	160	30	C	4		Precipitate extracted; tensile loss 16%
	70-80	940	B	21		Softened
POLYBUTA- DIENE RUB- BERS						
Acushnet						
BWK 422	160	30	C	4		Precipitate extracted, tensile loss 8.3%
BWK 640	160	30	C	4		Precipitate extracted, tensile loss 41.9%
BWK 650	160	30	C	4		Precipitate extracted, tensile loss 33.6%
BWK 651	160	30	C	4		Light precipitate ex- tracted, no strength loss; these are similar to Phillips compound No. 4705
Stillman EX 904-90 (Hydropol)	160	30	D	4		20% volume swell, tensile loss 77.5%, brittle
FLUOROMIL- ICOTENE RUB- BERS						
LB 53	55-60	30	D	15		Decomposed
Huhtan 88T80-33GT	160	30	C	4		Precipitate extracted, tensile loss 73.8%

^a - Definitions of ratings are given on page 4-14.

TABLE 4.2 (CONT)
COMPATIBILITY OF NONMETALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE: DEGREES FAHRENHEIT	STATIC EXPOSURE				REMARKS
		TIME IN DAYS		Liquid	Vapor	
		RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE
<u>ELIJUORO RUBBERS</u>						
Viton A	55-60	30	D	11		Decomposed
Viton B	55-60	30	D	11		Dissolved
Kel-F Elastomer	55-60	30	D	11		Dissolved
Flonel	55-60	30	D	15		
<u>MISCCELLA- NEOUS RUBBERS</u>						
Garlock 800	55-60	90	D	10		Fuel yellow, crystals on specimen
Garlock 33	55-60	90	C	10		Fuel discolored yellow
Buna N	55-60	30	D	11		Sample blistered
Neoprene	55-60	90	D	10		Fuel discolored red, softened 30%
Cohrlastic 500	55-60	90	D	10		Hardened
Hypalon 30	55-60	90	D	10		Black particles in fuel
<u>LUBRICANTS</u>						
UDMH Lube	70-80	1 ^b	C	4		Some washed off
S #58-M	70-80	1 ^b	C	4		Some washed off
Lox Salt	70-80	1 ^b	C	4		Some washed off
ANDOX-C	70-80	1 ^b	C	4		Some washed off

^a - Definitions of ratings are given on page 4-14.^b - Dynamic tests with Parco 805-70 butyl rubber O-rings.

TABLE 4.2 (CONT)
COMPATIBILITY OF NONMETALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE						REMARKS	
		TIME IN DAYS		TIME IN DAYS		TIME IN DAYS			
		RATING ^a	REFERENCE	RATING ^a	REFERENCE	RATING ^a	REFERENCE		
<u>LUBRICANTS CONT</u>									
DC-11	70-80	1 ^b	C	4				Some washed off	
	70-80	14	C	4	14	C	4	Washed off in liquid, partly in vapor	
Microssal 100-1 (dry lube)	70-80	1 ^b	B	4				Compatible	
Rockwell Nordstrom 980	70-80	1 ^b	C	4				Some washed off	
DC-55	70-80	1 ^b	C	4				May affect butyl rubber	
	70-80	14	C	4	14	C	4	Washed off in liquid, partly in vapor	
DC-HI Vacuum	70-80	1 ^b	C	4				May affect O-ring	
	65-80	90	C	10				Some washed off	
	70-80	14	C	4	14	C	4	Washed off in liquid, partly in vapor	
Kel-F 90	55-80	30	D	11				Reacted	
Molykote Z	55-80	30	D	11				Reacted and evolved gas	
Drilube 703	55-80	30	D	11				Gas evolved	
Rayco-32	55-80	30	D	11				Decomposed	
QC-2-0026 QC-2-0053	55-80	30	D	11				Dissolved	
Electrofilm 65-C	55-80	30	D	11				Sealed	

a - Definitions of ratings are given on page 4-14.

b - Dynamic tests with Parco 805-70 butyl rubber O-rings.

TABLE 4.2 (CONT)
COMPATIBILITY OF NONMETALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE					
		TIME IN DAYS		TIME IN DAYS		TIME IN DAYS	
		RATING ^a	REFERENCE	RATING ^a	REFERENCE	RATING ^a	REFERENCE
<u>LUBRICANTS (CONT)</u>							
TMEF-1,2,3	55-80	30	D	11			Broken up
Polyglycol Oil	70-80	14	C	1,4			Some washed off
I-1111	70-80	14	D	4			2 phases, fuel turned orange
<u>THREAD SEALANTS</u>							
Reddy Lube 100	70-80	14	A	4			Satisfactory
200	70-80	14	A	4			Satisfactory
Water Glass-Graphite	70-80	14	A	4			Satisfactory
Vynax A	70-80	14	C	4			Some washed off
<u>POTTING COMPOUNDS</u>							
PR 1433	55-80	30	D	11			Dissolved
RTV-30	55-80	30	D	11			Shrinks 6.9%, softened 24%
Epon 838	55-80	30	D	11			Broke apart
Paraplex P-43	55-80	30	D	11			Decomposed
Proseal T93	55-80	30	D	11			Dissolved
Fairprene 5150	55-80	30	D	11			Swollen; became brittle

a - Definitions of ratings are given on page 4-14.

TABLE 4.2 (CONT)
COMPATIBILITY OF NONMETALS WITH 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FAHRNHEIT	STATIC EXPOSURE				REMARKS	
		LIQUID		VAPOR			
		TIME IN DAYS	RATING ^a	TIME IN DAYS	RATING ^a		
<u>POTTING COMPOUNDS (CONT)</u>							
Crystal M & CF	55-80	30	C	11		Limited use	
<u>ADHESIVES</u>							
Armstrong A-8	55-80	90	A	10		Satisfactory	
EC 847	55-80	30	D	11		Fall apart	
HT 424	55-80	30	A	10		Satisfactory	
<u>CERAMICS</u>							
Temporell	55-80	90	A	10		Satisfactory	
Bauereisen P-1	55-80	90	A	10		Satisfactory	
Bauereisen 31	55-80	90	A	10		Satisfactory	
Bauereisen 47	75	-	C	4		Partly removed within 1 hour, limited service	
Rockflux	75	-	A	4		Satisfactory for 10.5 hours	
<u>PAINTS</u>							
Epoxy No. 1	55-80	30	D	11		Dissolved	
Modified Epoxy No. 5	55-80	30	D	11		Edges swollen	

a - Definitions of ratings are given on page 4-14.

TABLE 4.2 (CONT)
COMPATIBILITY OF NONMETALS V 'H 50/50 FUEL BLEND

MATERIAL	TEMPERATURE DEGREES FARENNHEIT	STATIC EXPOSURE				REMARKS	
		LIQUID		VAPOR			
		TIME IN DAYS RATING ^a	REFERENCE	TIME IN DAYS RATING ^a	REFERENCE		
<u>PAINTS - (CONT)</u>							
Epoxy No. 1	55-60	30	D	11		Stripped off	
Epoxy No. 9	55-60	30	D	11		Dissolved	
Epoxy No. 6809	55-60	30	D	11		Pealed off	
Alkyd No. 4	55-60	30	D	11		Stripped off	
Polyurethane	55-60	30	D	11		Stripped off	
Acrylic Hi- tackalumines	55-60	30	D	11		Dissolved	
Vinyl	55-60	30	D	11		Blistered	
Primer MIL-P-8880	55-60	30	D	11		Stripped off	
Catalac							
Primer and Finish	100	-	D	4		Prime coat lifted im- mediately and other within 7 days	
Improved	100	-	D	4		Paint lifted within 2 minutes	
Tygon K	100	-	D	4		Paint blistered within 1 hour	
Co-Polymer P-300 G	100	-	D	4		Paint washed off within 3 minutes	
CA 9747 Primer	100	-	D	4		Blistered and dis- solved within 10 min- utes	
Corrosion Clear 561	100	-	D	4		Blistered within 1 hour	

a -- Definitions of ratings are given on page 4-14.

4.3 EFFECTS OF FUEL BLEND ON MATERIALS OF CONSTRUCTION

Table 4.3 is a list of construction materials showing the compatibility results of short exposure to fuel blend liquid spillage, fuel blend vapors, and watered fuel blend. Details of these tests are given in Reference 4. Coatings and/or surface treatments were applied to various materials to ascertain life expectancy. Of the organic coatings, Sauereisen 47 exhibits the best resistance. Rockflux, an inorganic concrete coating material having a viscous consistency when mixed with water, appears to be resistant to the 50/50 fuel blend. However, bare concrete is unaffected by the fuel blend.

TABLE 4.3

COMPATIBILITY OF CONSTRUCTION MATERIALS WITH
50/50 FUEL BLEND

Material	Temperature (°F)	Exposure Time	Remarks
Birch Wood	75	2 hr 30 min	Wood grain split
Concrete			
Bare	75	13 hr	No visual effect
Coated with water glass	75	1 hr 30 min	Water glass crystallized and powdered off
Coated with water glass and floor enamel (Esco Brand 41138)	75	1 hr 15 min	Paint blistered
Coated with water glass and Chex-Wear floor enamel	75	6 min	Paint blistered
Coated with Rockflux	75	10 hr 30 min	No visual effect
Mild Steel Coated with			
Tygon K paint	75	1 hr	Paint blistered
Catalac improved paint	75	1 hr 30 min	Grainy appearance; lifted when totally immersed
Co-Polymer P-200G	75	3 min	Paint was removed
Sauereisen 47 (4 coatings)	75	7 hr	First coating was removed in one hour; blistered but did not penetrate 4 coatings
CA 9747 Primer paint	75	10 min	Blistered and discolored
Corrosite Clear 581	75	1 hr 15 min	Blistered

4.4 EFFECTS OF METALS ON FUEL BLEND DECOMPOSITION

To determine the effects of materials on fuel decomposition, portions of unwelded, welded, brazed, and soldered metal specimens were sealed in Pyrex glass ampules with a small quantity of 50/50 fuel blend and placed in test for 14 days at 160°F. Blanks containing only fuel blend also were included as controls. After test, a weight loss of the fuel blend was indicative of decomposition. Details of this test are presented in Reference 2. The metals tested are shown in Table 4.4. Although the data obtained with this procedure is inconclusive, the specimens do not show signs of attack or discoloration and the fuel blend does not show signs of discoloration. Since the fuel samples subjected to spectral analyses are no worse than the control samples, no decomposition is attributable to the metals.

TABLE 4.4

METALS TESTED FOR DETERMINING 50/50 FUEL BLEND DECOMPOSITION

Aluminum Alloys

2014-T6	manual welded and unwelded
2014-T6	machine welded
5086 H-36	manual welded and unwelded
5456 H-321	manual welded and unwelded
6061-T6	manual welded, brazed, and unwelded

Stainless Steels

304L	annealed, manual welded and unwelded
321	annealed, manual welded and unwelded
347	annealed, manual welded, microbrazed, and unwelded
410	H & T, manual welded and unwelded

A-Nickel

manual welded and unwelded

4.5 EFFECTS OF CONTAMINANTS ON FUEL BLEND

Filings of 2014 aluminum alloy and types 304, 316, and 347 stainless steels were exposed to 50/50 fuel blend at 160° F for 14 days to determine the potential effects of contaminants on the fuel blend picked up during systems manufacturing. The metal filings were sealed in Pyrex glass ampules with fuel blend and, after test, the fuel blend weight loss indicated decomposition (References 2 and 4). Although the data obtained from each test is inconclusive, no visual changes are apparent in either the fuel blend or the metal filings. Also, no positive pressure was detected upon opening the test ampules.

Tests were made with 6061 aluminum alloy, type 347 stainless steel shavings, and lint exposed to the 50/50 fuel blend contained in glass flasks fitted with reflux condensers (Reference 2). After one week at 160° F, no visual changes were detected in either the fuel or the metal, and spectral analyses of the fuel indicated no decomposition. With lint, the analysis of the fuel blend is hampered by the absorption of the lint dye; however, observations during test indicate no decomposition.

SECTION 5.0

MATERIALS COMPATIBILITY, N₂O₄

SECTION 5.0

MATERIALS COMPATIBILITY, N_2O_4 5.1 EFFECTS OF N_2O_4 ON METALS

As a result of laboratory tests interpreted on the basis of practical experience, the individual metals are placed into the classifications described in Section 4.0, page 4-1 of this handbook.

Table 5.1 contains pertinent compatibility data, references, and ratings of several metals and metal alloys.

5.1.1 Aluminum Alloys

Aluminum alloys behave as stable materials because they are covered with a naturally occurring thin oxide film that is highly resistant and protective. These alloys have been known to withstand nitric acid above 82% by weight. Moist N_2O_4 produces 60% to 70% by weight nitric acid. The radical difference between aluminum alloys and stainless steel alloys is that the corrosion rate of stainless steel alloys in nitric acid decreases as the concentration is reduced, whereas the opposite is true of aluminum alloys.

Certain aluminum alloys exhibit higher corrosion rates when exposed to N_2O_4 containing varying water contents. The zinc-bearing 7075 aluminum alloy corrodes at a faster rate than the copper-bearing 2024 aluminum alloy. Under identical test conditions, both alloys corrode faster than 5052 and 3003 aluminum alloys; 3003 aluminum alloy exhibits the lowest corrosion rate (Reference 1). The evidence indicates that the purer the aluminum, the less the corrosion in N_2O_4 containing increased water content. The significance is not apparent until N_2O_4 contains greater than 0.3% water.

The alloys tested cover a variety of casting and wrought alloys that are characterized by good strength, weldability, formability, and corrosion resistance.

There was no major difference in mechanical properties as a result of the testing in the presence of N_2O_4 having a water content of 0.2% maximum and up to a temperature of 165°F. There was no effect on the alloy tested when in contact with Teflon (Reference 16). The criterion for resistance of the alloys is the water content of the N_2O_4 .

The application of a heavier oxide film by electrolytic means or chemical conversion does not result in a major difference in corrosion regardless of the water content of the N_2O_4 .

5.1.2 Stainless Steels

The stainless steels mentioned in Table 5.1 are a cross-section of alloys that are durable, heat- and corrosion-resistant, and non-contaminating. They contain at least 12% chromium, often 7% or more nickel, and additives such as molybdenum, columbium, and titanium. Included are the hardenable heat-resistant alloys which lack nickel. All these alloys are resistant to N_2O_4 oxidizing conditions, including the presence of nitric acid.

Maximum corrosion resistance of the stainless steels can be attained by proper fabrication techniques. The effect of welding, brazing, and improper heat treatments on the corrosion resistance of stainless steels is well known. Included in Table 5.1 are specimens prepared by means of acceptable fabrication procedures.

A limited number of N_2O_4 metal corrosion tests conducted by the Nitrogen Division of Allied Chemical Corporation (Reference 16) indicates that the presence of Teflon can increase the corrosion rate of type 304L SS. However, corrosion rates of 304L SS with and without Teflon are less than 1 MPY with specification-grade N_2O_4 at 185°F for 70 days and with N_2O_4 containing as much as 2% water at 115°F for 109 days.

Under the test conditions stated in Table 5.1, regardless of the source of information, there is no major difference in the mechanical properties of stainless steel. This includes welded, microbrazed, tin-soldered, and silver-brazed joints. Tin solder and silver brazing are readily attacked by dilute nitric acid; therefore, this fabrication procedure must be used with discretion because severe corrosion could occur with increased water content of the N_2O_4 .

5.1.3 Ferrous Alloys

The ferrous alloys are not known to have high resistance to oxidizing conditions and their use is a matter of economics. This is specifically true when nitric acid is the oxidizer; however, at high concentrations of nitric acid, the corrosion rate reaches a low value. The ferrous alloys are unaffected by N_2O_4 having 0.4% water maximum up to 165°F. A limited number of tests conducted by the Nitrogen Division of Allied Chemical Corporation (Reference 16) indicates that the presence of Teflon can increase the corrosion rate of carbon steel. However, corrosion rates of ASTM-A285 grade C are less than 1 MPY when exposed to specification-grade N_2O_4 at 115°F for 109 days and 165°F for 70 days.

5.1.4 Nickel Alloys

In general, oxidizing conditions promote corrosion of nickel alloys. Nickel can protect itself against certain forms of attack by developing a passive oxide film; thus, oxidizing conditions do not always accelerate the corrosion of nickel. While these alloys show good resistance

to dry N₂O₄, caution is advised in their use with moist N₂O₄. An exception to this is Inconel which has good corrosion resistance to oxidizing conditions.

5.1.5 Titanium Alloys

Commercially pure titanium is outstanding among structural materials in its resistance at ordinary temperatures to oxidizing conditions. Titanium, when passivated, is the noble metal in a galvanic couple with all structural alloys except Monel and stainless steels. The titanium alloys are generally less resistant to corrosion than commercially pure titanium. Care has been exercised in exploring new combinations of titanium alloys and corrosive mediums. This is due to its pyrophoric properties in RFNA and its impact sensitivity with liquid oxygen and fluorine. However, it is only in the case of liquid oxygen that the reaction may propagate and completely consume the titanium. In most cases, even though ignition occurs, the damage is not significantly greater than that resulting from the impact alone. A smooth, surgically clean titanium surface minimizes the reaction (Reference 22). The data in Table 5.1 shows that the titanium alloys are virtually unaffected by N₂O₄ and moist N₂O₄ up to 25% by weight. No ill effects occur when coupled to 2014-T6 aluminum alloy in N₂O₄. (See Propellant Handling, Section 6.0, for additional data substantiating the use of titanium with N₂O₄.) All testing to date indicates that titanium alloys are satisfactory for use with N₂O₄.

5.1.6 Magnesium Alloys

Magnesium alloys corrode in N₂O₄ and corrosion products form on the surface of the metals.

5.1.7 Copper Alloys

Berylico 25 exhibits a corrosion rate of less than 1 MPY; however, because corrosion products form on the surface of this alloy and are easily removed, a "C" rating is assigned.

5.1.8 Cobalt Alloys

Haynes Stellites No. 6K and 25 exhibit good corrosion resistance with N₂O₄.

5.1.9 Platings

Gold-plated Berylico 25 exhibits a corrosion rate less than 1 MPY; however, because corrosion products form on the surface and are removed easily, a "C" rating is assigned. Non-porous chromium, nickel plating, and electroless nickel are satisfactory for N₂O₄ service.

5.1.10 Conversion Coatings

There is evidence to show that sulfuric acid anodize, Hardas and iridite aluminum conversion coatings are resistant to N_2O_4 exposure.

5.1.11 Miscellaneous Alloys

Silver solder, as reported in Reference 10, becomes badly pitted N_2O_4 after one month and exhibits a high corrosion rate. Tantalum exhibits good corrosion resistance to N_2O_4 .

TABLE 5.1
COMPATIBILITY OF METALS WITH N₂O₄

MATERIAL	TEMP. DEG F	TIME HOUR	STATIC EXPOSURE								
			LIQUID			VAPOR			INTERFACE		
			TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE
ALUMINUM ALLOYS											
1100-O	55-60	90	A	15,11 19							
	100	7	A	18							
2014-T6 Sheet											
Unwelded	55-60	90	A	15,11	90	A	15,11	90	A	15	
Welded	55-60	90	A	15,11	90	A	15,11				
	63-67	14	A	4							
Spotwelded	55-60	180	D	15,11	180	D	15,11				
2014-T6 Extrusion											
Unwelded	55-60	90	A	15							
Stressed to 50,000 psi	55-60	90	A	15							
Welded	55-60	90	A	15	90	A	15				
Stressed to 30,000 psi	55-60	90	A	15							
	55-60	30	A	15							
Stressed to 50 % and 80% Yield	55-60	15	A	15							
2024-O	55-65	63	A ^b	19	63	A ^b	19	63	A	19	
	100	7	A	1,19							
	140	11	A	19							
	150	7	B	14	7	A	14				
	150	7	A	14	7	A	14				

^a - Definitions of ratings are given on page 4-1.^b - Predicted rating from interface data.

TABLE 5.1 (CONT)

COMPATIBILITY OF METALS WITH N_2O_4

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE						REMARKS	
		LIQUID		VAPOR		INTERFACE			
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE		
ALUMINUM ALLOYS (CONT)									
2219-T81 Welded and Unwelded	55-60	90	A	15				No effect, up to 0.3% H_2O	
3003-H14	100	7	A	1,19	7	A	14	Up to 0.4% H_2O Up to 0.6% H_2O	
5052-0	100	7	A	1,19				"B" rating at 0.3% to 1.0% H_2O	
5086-H34 Unwelded	140	29	B	19					
	15	56	A	16				Up to 0.4% H_2O	
	70	27	A	16				Up to 0.8% H_2O	
	70	27	B	16				1.6% H_2O	
	70	27	C	16				3.2% H_2O	
	115	109	A	16				Up to 0.5% H_2O	
	115	109	B	16				1.0% H_2O	
	115	109	C	16				2.0 to 3.0% H_2O	
	120	27	A	16				Up to 0.4% H_2O	
	120	27	B	16				0.8% H_2O	
	120	27	C	16				1.6% H_2O	
	120	27	D	16				3.2% H_2O	
	165	70	A	16					
	165	70	B	16				0.5% H_2O	
	165	70	C	16				1.0% H_2O	
	165	70	D	16				2.0 to 3.0% H_2O	
Welded	15-165	27	A	16				<0.4% H_2O	
	15-165	27	B	16				0.4 to 3.2% H_2O	

a — Definitions of ratings are given on page 4-1.

TABLE 5.1 (CONT)

COMPATIBILITY OF METALS WITH N₂O₄

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE									
		LIQUID			VAPOR			INTERFACE			
		TIME IN DAYS	RATING ^a	REFERENCE	TIME L/DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	REMARKS
<u>ALUMINUM ALLOYS (CONT)</u>											
5086-H36											
Unwelded	63-67	90	A ^b	4	90	A ^b	4	90	A	4	
Welded	63-67	14	A	4	90	A ^b	4	90	A	4	
5254-F	63-67	90	A ^b	4	90	A ^b	4	90	A	4	
5456-H24	55-60	90	A	15							
Welded and Unwelded											
5456-H321											
Unwelded	55-60	90	A	15							0.2% H ₂ O
	63-67	14	A	4							
Stressed to 30,000 psi	55-60	30	A	15							0.2% H ₂ O
Welded	55-60	30	A	15	90	A	15				0.6% H ₂ O
Stressed to 20,000 psi	55-60	30	A	15							0.3% H ₂ O
6061-T6	55-60	90	A	10	90	A ^b	4	90	A	4	
Unwelded	63-67	90	A ^b	4	90	A ^b	4	90	A	4	
	130	30	A	19							0.5% H ₂ O
	100	7	A	18							0.3% H ₂ O
	150	7	A	14	7	A	14				Up to 0.6% H ₂ O
Welded	55-60	90	A	15							
	63-67	14	A	4							
6066	63-67	90	A ^b	4	90	A ^b	4	90	A	4	
7075-T6	55-60	90	A	15							0.6% H ₂ O

a - Definitions of ratings are given on page 4-1.

b - Predicted rating from interface data.

TABLE 5.1 (CONT)

COMPATIBILITY OF METALS WITH N_2O_4

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE									
		TIME IN DAYS			LIQUID			VAPOR			INTERFACE
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	REMARKS
<u>ALUMINUM ALLOYS (CONT)</u>											
7075-0	100	7	A	1,18							"B" rating at 0.2% H_2O ; "C" rating above 0.5% H_2O
	150	7	A	14	7	A	14				0.3% H_2O
	150	7	B	14	7	B	14				
	55-65	30	A ^b	19	30	A ^b	19	30	A	19	
356-T6	55-60	90	A	15							0.2% H_2O
	55-65	30	A ^b	19	30	A ^b	19	30	A	19	
Tens 50	63-67	90	A ^b	4	90	A ^b	4	90	A	4	
<u>STAINLESS STEELS</u>											
302	100	7	A	19							
303	63-67	90	A ^b	4	90	A ^b	4	90	A	4	
	100	7	A	19							
304	55-65	63	A ^b	19	63	A ^b	19	63	A	19	
304L											
Unwelded	55-60	90	A	15							0.2% H_2O
	63-67	14	A	4							
	15-165	27	A	16							Up to 3.2% H_2O Incl
Welded	63-67	14	A	4							
316	63-67	90	A ^b	4	90	A ^b	4	90	A	4	
	63-67	90	A ^b	4	90	A ^b	4	90	A	4	

a — Definitions of ratings are given on page 4-1.

b — Predicted rating from interface data.

TABLE 5.1 (CONT)

COMPATIBILITY OF METALS WITH N₂O₄

MATERIAL	TEMPERATURE DEGREES FARENNHIT	STATIC EXPOSURE											
		LIQUID				VAPOR				INTERFACE			
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATIO ^b	REFERENCE	TIME IN DAYS	RATING ^b	REFERENCE	TIME IN DAYS	RATING ^b	REFERENCE
STAINLESS STEELS (CONT.)													REMARKS
321													
Unwelded	65-80	180	A	15	180	A	15	180	A	15			
Welded	65-80	180	A	15									Up to 3.0% H ₂ O
	65-87	14	A	4									
347													
Unwelded	65-80	180	A	15									
	65-87	90	A ^b	4	90	A ^b	4	90	A	4			
		30	A	10									
		100	A	15									10% H ₂ O
Welded	65-80	180	A	15									
	65-87	14	A	4									
17-4 PH Cond. A	65-87	90	A ^b	4	90	A ^b	4	90	A	4			
17-4 PH (H1100)	100	10	A	14									Up to 0.3% H ₂ O
17-7 PH	65-85	30	A ^b	10	30	A ^b	10	30	A	10			
17-7 PH TH 950	100	14	A	14									Up to 3.0% H ₂ O
17-7 PH RH 950	100	14	A	10									Up to 0.3% H ₂ O
PH 17-7 Mo Cond. A	65-87	90	A ^b	4	90	A ^b	4	90	A	4			
	13-103	27	A	10									Up to 3.0% H ₂ O
AM 350 Cond. H	65-87	90	A ^b	4	90	A ^b	4	90	A	4			

^a — Definitions of ratings are given on page 4-1.^b — Predicted rating from interface data.

TABLE 5.1 (CONT)

COMPATIBILITY OF METALS WITH N_2O_4

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE											
		TIME IN DAYS			LIQUID			VAPOR			INTERFACE		
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE
STAINLESS STEELS (CONT)													
AM 350 Ann.	100	10	A	18									10% H_2O
A 286 Ann.	55-60	90	A	15									
	100	7	A	14									Up to 0.5% H_2O
410 H & T	63-67	90	A ^b	4	90	A ^b	4	90	A	4			
Welded	63-67	14	A	4									
410 (Rc 41)	100	7	A	14									Up to 1% H_2O
	150	7	A	14									
416	55-65	30	A ^b	19	30	A ^b	19	30	A	19			
440 C	63-67	90	A ^b	4	90	A ^b	4	90	A	4			
Ann.	100	7	A	14									Up to 0.6% H_2O
FERROUS ALLOYS													
ASTM A-285 (Grade C)	15	27	A	16									Up to 3.2% H_2O Incl
	70	27	A	16									Up to 0.6% H_2O Incl
	70	27	B	16									1.6 to 3.2% H_2O
	120	27	A	16									Up to 0.4% H_2O Incl
	120	27	B	16									0.8% H_2O
	120	27	C	16									>0.8% H_2O to 3.2% Incl
	165	27	A	16									Up to 0.4% H_2O Incl
	165	27	B	16									0.8% H_2O
	165	27	C	16									>0.8% H_2O to 3.2% Incl

a - Definitions of ratings are given on page 4-1.

b -- Predicted rating from interface data.

TABLE 5.1 (CONT)
COMPATIBILITY OF METALS WITH N₂O₄

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE									
		LIQUID			VAPOR			INTERFACE			
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	REMARKS
FERROUS ALLOYS (CONT)											
1030	55-60	90	A	15							0.25 H ₂ O
	130	30	A	18							
8630	140	30	A	18							
NICKEL ALLOYS											
Inconel	55-65	22	A ^b	18	22	A ^b	18	22	A	18	
Mosel ^c	55-65	63	A ^b	18	63	A ^b	18	63	A	18	
"A" Nickel ^c Welded and Unwelded	63-67	14	A	4							
NI Spec C	55-60	30	A	18							0.25 H ₂ O
Nivar	55-60	30	A	10							
TITANIUM ALLOY											
B130 VCA	55-60	90	A	15				--			
C130 AV	55-60	90	A	15							Up to 3.7% H ₂ O
	70-105	27	A	15							Up to 3.7% H ₂ O
TSA	70-105	37	A	15							Up to 35% H ₂ O
T1 GSA	100	14	A	18							2% H ₂ O, discoloration in vapor
RC 130 AM	100-150							14	A	18	
A110 AT	55-65 ^a	7	A ^b	10	7	A ^b	10	7	A	10	

a -- Definitions of ratings are given on page 4-1.

b -- Predicted rating from interface data.

c -- These alloys are highly susceptible to corrosion in nitric acid.

TABLE 5.1 (CONT)
COMPATIBILITY OF METALS WITH N_2O_4

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE									
		LIQUID			VAPOR			INTERFACE			
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE	REMARKS
MAGNESIUM ALLOYS											
HM 21A TB ^c	55-60	30	A	15							3.0% H_2O
AZ 31C ^c	55-60							60	D	10	"D" rating because of slight corrosion products
AM 100A ^c	55-65							60	D	10	"D" rating because of slight corrosion products
COPPER ALLOYS											
Beryllio 25 ^b	63-67							60	C	4	Corrosion products
COBALT ALLOYS											
Haynes Stellite											
6X	55-65	60	A ^b	10	60	A ^b	10	60	A	10	
25	63-67	90	A ^b	4	90	A ^b	4	90	A	4	
PLATING											
Cadmium	55-60	-	D	15							
Chromium (non-porous)	55-60	-	A	15							
Copper ^b	55-60	-	C	15							
Gold on Beryllio 25	63-67							30	C	4	Plating porous, corrosion products

a - Definitions of ratings are given on page 4-1.

b - Predicted rating from interface data.

c - These alloys are highly susceptible to corrosion in nitric acid.

TABLE 5.1 (CONT)

COMPATIBILITY OF METALS WITH N_2O_4

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE						REMARKS	
		LIQUID		VAPOR		INTERFACE			
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE		
<u>PLATINGS (CONT)</u>									
Nickel									
Electrolytic (non-porous)	55-60	-	A	15					
Electroless	100	T	A	15					
Silver	55-60	-	D	15					
Zinc	55-60	-	D	15					
<u>COATINGS ON ALUMINUM ALLOYS</u>									
Iridia									
2014-T6									
Welded	55-60	30	A	10,11				0.369% H_2O	
	55-60				90	A	10,11		
Unwelded	55-60				30	A	10	2.12% H_2O	
2319-T81	55-60	30	A	10				1.38% H_2O	
Welded									
1458-T34	55-60	90	A	15					
Welded									
6061-T6	55-60	90	A	15					
Welded									
Sulfuric Acid Anodize									
7075-T6	100	T	B	15				The coatings do not improve resistance to oxidizer; data too scattered for conclu- sive evidence	
A356	100	T	B	15					
	100	T	B	15					

a - Definitions of ratings are given on page 4-1.

TABLE 5.1 (CONT)

COMPATIBILITY OF METALS WITH N₂O₄

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE						REMARKS	
		LIQUID		VAPOR		INTERFACE			
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE		
COATINGS ON ALUMINUM ALLOYS (CONT)									
2014-T6 Al	63-67						30	A	
Hardas Anodize								4	
2014-T6 Al	55-60	30	A	15					
Hard Coat (Banfurize)									
2014	100	7	B	18					
A 354	100	7	A	18					
7075	100	7	B	18					
MISCELLAN- EYOUS									
Microseal 100-1 on AM 100A Magnesium	63-67						100	D	
Microseal 100-1 CG on AZ 31C Magnesium	63-67						75	D	
Microseal 100-1 on 2014-T6 Al	63-67						100	A	
Silver Solder ^c	55-60	30	D	10					
Tantalum	55-65	30	A ^b	10	30	A ^b	10	Pitting	

a -- Definitions of ratings are given on page 4-1.

b -- Predicted rating from interface data.

c -- These alloys are highly susceptible to corrosion in nitric acid.

TABLE 5.1 (CONT)
COMPATIBILITY OF METALS WITH N₂O₄

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE					
		LIQUID		VAPOR		INTERFACE	
		TIME IN DAYS	RATING*	REFERENCE	TIME IN DAYS	RATING*	REFERENCE
<u>BRAZING AND SOLDERING</u>							
6061-T6 Al brazed with T18 filler	63-67	14	A	4			
303SS sol- dered with pure Tin	63-67	14	A	4			
347SS silver brazed with Easy Flo per QQ-S-561 Class 4	63-67	14	A	4			
347SS micro- brazed AMM 4775	63-67	14	A	4			
<u>METAL COUPLES</u>							
2014-T6 Al coupled to Teflon	63-67				30	A	4
2014-T6 Al bolted to GA1-4V Ti- tanium	50-60	90	A	15			0.2% H ₂ O
2014-T6 Al bolted to 321SS	50-60	90	A	15			0.2% H ₂ O
2014-T6 Al welded to 6061-T6 Al	63-67	14	A	4			

a - Definitions of ratings are given on page 4-1.

TABLE 5.1 (CONT)
COMPATIBILITY OF METALS WITH N₂O₄

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE						REMARKS	
		LIQUID		VAPOR		INTERFACE			
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE		
METAL COUPLES (CONT)									
304 SS/ Teflon/321 SS bolted	55-90	30	A	16				0.5% H ₂ O	
304L coupled with Teflon	115	90	A	16				Up to 1.0% H ₂ O Incl	
	115	109	A	16				Up to 2.0% H ₂ O Incl	
	165	70	A	16					
	165	70	B	16				0.5 to 3.0% H ₂ O Incl	
	63-87				30	A	4	Tape or bar Teflon had no effect	
ASTM A-285 (Grade C)									
In presence of Teflon	115	90	A	16				Up to 1.0% H ₂ O Incl	
	115	109	A	16				>0.1% to 2.0% H ₂ O Incl	
	115	109	B	16				3.0% H ₂ O	
	165	70	C	16					
	165	70	A	16				0.5 to 1.0% H ₂ O Incl	
	165	70	B	16				2 to 3% H ₂ O Incl	
	165	70	C	16					

a — Definitions of ratings are given on page 4-1.

5.2 EFFECTS OF N₂O₄ ON NONMETALS

Table 5.2 contains compatibility data, references, and the ratings of several nonmetals exposed to N₂O₄. The ratings are identical with those described in Section 4.0, page 4-13, on the 50/50 fuel blend materials compatibility.

An intimate knowledge of the behavior of plastics, rubbers, and elastomers under the conditions of their intended use is a prerequisite for engineering design. Being chiefly organic, the nonmetals are generally sensitive to N₂O₄ and their mechanical properties in this environment are more susceptible to changes in a short range of temperature.

The chemical environment can act on these materials in several ways. The propellant can dissolve, attack, and decompose the material causing degradation, or it can completely destroy the material. Moreover, the propellant can extract some components, thereby altering physical properties, or it can be absorbed by the material and thus affect the strength. In addition, the chemical environment can affect the dimensional stability and finish appearance without seriously affecting the mechanical properties. The nonmetals tested embrace a wide variety of chemical and physical structures and, as such, geometrical factors, methods of fabrication, and similar variables can greatly influence the behavior of a part fabricated from any of the nonmetals shown in Table 5.2.

For example, many of these nonmetals can be used as gaskets or seals where a definite compression set limitation and, probably volume change limitation, is required for sealing. The gasket or seal can be enclosed between two metal surfaces with only a small portion exposed to the medium. The swelling characteristics of this type exposure differ in magnitude and importance when compared with the swelling obtained from complete immersion in the medium where volume change is magnified. Tensile properties play a small role in the application of the material for a gasket; when used as an O-ring, tensile properties are important. Therefore, the application of any of the nonmetals must be weighed in terms of the physical properties desired.

5.2.1 Plastics

The Teflon and Teflon products exhibit the best resistance to N₂O₄; however, N₂O₄ permeates and is absorbed by Teflon. The important considerations are the retention of properties after outgassing the N₂O₄. Teflon swells approximately 5% before outgassing and returns to its original volume after outgassing.

The polyethylenes absorb N₂O₄ and increase in brittleness with time. Certain polyethylenes show good resistance to N₂O₄ for periods up to 30 days.

5.2.2 Elastomers

The fluororubbers swell considerably in N_2O_4 and have a negative volume change after outgassing.

Phenolic resin-cured butyls and fluorosilicone rubbers show resistance to N_2O_4 . Even these are good for only short-term service.

5.2.3 Lubricants and Sealants

Reddy Lubes 100 and 200 and water glass/graphite mixture are satisfactory thread sealants. All the lubricants either react or wash off in N_2O_4 ; however, for assembly purposes, Nordcoseal greases can be used satisfactorily. Dry lubricants Molykote Z, Drilube 703, and Electrofilm 66 C are satisfactory for use with N_2O_4 .

5.2.4 Potting Compounds and Ceramics

Only Sauereisen P-1, a ceramic, exhibits satisfactory resistance to N_2O_4 . There are no potting compounds satisfactory for service with N_2O_4 .

5.2.5 Adhesives

Testing to date indicates that there are no adhesives satisfactory for service with N_2O_4 .

5.2.6 Paints

Testing to date indicates that there are no paints satisfactory for service with N_2O_4 .

5.2.7 Miscellaneous

Graphitar 2 and 50 are satisfactory for service with N_2O_4 .

TABLE 5.2
COMPATIBILITY OF NONMETALS WITH N₂O₄

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE						REMARKS	
		LIQUID		VAPOR		TIME IN DAYS	REFERENCE		
		TIME IN DAYS	RATING ^a	TIME IN DAYS	RATING ^a				
PLASTICS									
Polytetrafluoroethylene									
Teflon (TFE)	55-60	30	B	11				1% to 3% H ₂ O	
	63-67	30	A	4					
	70-80	100	B	1,11				Softened 20%	
Teflon filled with graphite	55-60	90	A	15					
Teflon filled with molydisulfide	55-60	90	A	15					
Teflon filled with asbestos	55-60	90	A	15					
Armalon 7700 impregnated with Teflon fibers	55-60	90	A	15					
Armalon 7700B impregnated with Teflon fibers	55-60	90	A	15					
Fluorobestos filled with asbestos	55-60	30	B	11				Increased hardness 39%	
TFE-felt 7550	55-60	30	D	11				Sample coming apart	

a - Definitions of ratings are given on page 4-14.

TABLE 5.2 (CONT)

COMPATIBILITY OF NONMETALS WITH N_2O_4

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE						REMARKS
		LIQUID		VAPOR		TIME IN DAYS	RATING ^a	REFERENCE
		TIME IN DAYS	RATING ^a	TIME IN DAYS	RATING ^a			
PLASTICS (CONT)								
Fluoro-green filled with ceramic	55-60	30	A	15				
Fluorinated Propylene Co-polymer								
Teflon (FEP)	55-60	30	C	11				
	63-67	30	A	4				
	70-80	90	A	12				
	160	7	A	12				
Polychlorotrifluoroethylene								
Kel-F 300 Unplasticized	55-60	30	C	11				Up to 3% H_2O , sample discolored and softened 16%
	63-67	30	A	4				30% loss in strength
	70-80	70	C	1				Softened 76%
Annealed	55-60	30	C	11				Sample discolored and softened
Genetron								
GCX-3B	55-65	30	A	19				
XE-2B	55-65	30	A	19				
Trithene A	70-80	90	C	12				Hardened 12%
Polyethylene								
Low Density	55-60	30	C	11				Sample turned brown
Irradiated	55-60	30	C	15				Limited service
Hi Density	55-60	30	C	15				Limited service

a — Definitions of ratings are given on page 4-14.

TABLE 5.2 (CONT)
COMPATIBILITY OF NONMETALS WITH N_2O_4

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE					
		TIME IN DAY ^a		TIME IN DAYS		REMARKS	
		LIQUID RATING ^a	REFERENCE	VAPOR RATING ^a	REFERENCE		
PLASTICS (CONT)							
Polyvinyl							
Raythene N (irradiated)	55-60	30	D	10			Cracked
White and black in- sulation	63-67	30	A	4			Slight dimensional change
Polypropylene							
From Hercules	55-60	30	C	11			Sample turned green
Polyamide- nylon							
Eytel 101	55-60	30	D	11			Breaks apart
Polyester							
Mylar	55-60	30	D	11,12			
Laminates- Glass							
Silicone (composi- tion un- known)	55-60	30	D	11			Delaminated
Phenolic (composi- tion un- known)	55-60	30	C	11			Sample was bleached
Epoxy (composi- tion un- known)	55-60	30	D	11			Delaminated

a - Definitions of ratings are given on page 4-14.

TABLE 5.2 (CONT)
COMPATIBILITY OF NONMETALS WITH N₂O₄

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE						REMARKS	
		LIQUID		VAPOR		TIME IN DAYS REFERENCE ^a	TIME IN DAYS REFERENCE ^a		
		TIME IN DAYS REFERENCE ^a	RATING ^a	TIME IN DAYS REFERENCE ^a	RATING ^a				
PLASTICS (STONY)									
Polyester (composition unknown)	55-60	30	D	11				Delaminated	
Polyvinylidene Chloride									
Saran	55-60	30	D	11				Softened 17%	
Polyformaldehyde									
Delrin	55-60	30	D	11				Reaction	
Polycarbonate									
Lexan	55-60	30	D	11				Dissolved	
Polyvinyl Fluoride									
Teslar 30	63-67	30	A	4					
Polymethyl Methacrylate									
Plexiglass	55-60	30	D	11				Dissolved	
Polyvinyl Chloride									
Ultron	70-80	90	D	12				Surface tacky	
		160	7	D	12			Crumbled	

^a -- Definitions of ratings are given on page 4-14.

TABLE 5.2 (CONT)
COMPATIBILITY OF NONMETALS WITH N₂O₄

MATERIAL	TEMPERATURE DEGREES FAREHNHUT	STATIC EXPOSURE				REMARKS
		TIME IN DAYS RATING ^a	REFERENCE	TIME IN DAYS RATING	REFERENCE	
<u>PLASTICS (CONT)</u>						
Hydrocarbon Polymers						
Formulas 24-27 (polybutadiene)	70-80	7	D	24		Crumbled
Formula 39 (polyethylene)	70-80	30	C	20		20% volume swell, fair to good strength retention
Formulas 41-43 (isobutylene co-polymers)	70-80	7	D	24		Degraded
Formula 44 (isobutylene co-polymer)	70-80	30	D	20		Degraded
Formulas 45-52 (isobutylene co-polymers)	70-80	7	D	24		Degraded
Formula 53 (polyethylene + iso-butylene)	70-80	30	A	20		10% volume swell, good strength retention
Formula 68 (polyethylene + carbon black)	70-80	30	D	20		Degraded
Formulas 69-72 (polysisobutylenes)	70-80	7	D	24		Formulas 69 and 70 blistered or deteriorated, 71 and 72 swelled 145%

a - Definitions of ratings are given on page 4-14.

TABLE 5.2 (CONT)
COMPATIBILITY OF NONMETALS WITH N₂O₄

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE				REMARKS	
		LIQUID		VAPOR			
		TIME IN DAYS RATING ^a	REFERENCE	TIME IN DAYS RATING ^a	REFERENCE		
PLASTICS (CONT)							
Formulas 87-88 (iso- butylene co- polymer)	70-80	30	D	20		33% - 39% volume swell, poor elastomeric properties.	
Formula 100 (isobutylene co-polymer)	70-80	30	D	20		41% volume swell, poor elastomeric properties	
Formula 101 (isobutylene co-polymer)	70-80	30	B	20		17% volume swell, fair elastomeric proper- ties	
Formula 102 (isobutylene co-polymer)	70-80	30	D	20		33% volume swell, poor elastomeric properties	
Formulas 103-104 and 111 (isobu- tylene co- polymers)	70-80	7	D	20		27% - 30% volume swell, very poor to fair elastomeric proper- ties, formula 106 has volume swell 22%, but poor elastomeric properties	
DPDB 8100 (polyolefin)	70-80	7	D	20		49% volume swell, fair to good elastomeric properties	
Formula 110 (polyolefin)	70-80	7	D	20		49% volume swell, fair to good elastomeric properties	
Formula 116-117 (ethylene- propylene rubber)	70-80	7	D	20		<25% volume swell, rated "D" because of poor elastomeric properties	
Marlex 5003 (polyethylene + butene)	70-80	30	D	20		Because brittle	

a — Definitions of ratings are given on page 1-14.

TABLE 5.2 (CONT)
COMPATIBILITY OF NONMETALS WITH N₂O₄

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE						REMARKS	
		TIME IN DAYS		REFERENCE	TIME IN DAYS		REFERENCE		
		Liquid	Vapor		Rating ^a	Rating ^a			
BUTYL RUBBERS									
Enjay 268	55-60	-	D	15					
Enjay 551	55-60	30	D	11				Dissolved	
Hycar 2202	55-60	-	D	15					
Garlock 22	55-60	-	D	15					
Parker 805-70	55-65	7	D	19				Became tacky	
Parker XB-1235-10	70-80	7	D	1				63% volume swell, softened 77%	
FLUORO RUBBERS									
Parker XV-1235-2	70-80	7	D	1				500% volume swell, softened 85%	
XV-1235-5	70-80	7	D	1				430% volume swell, softened 92%	
TFNM-TFE (Trifluoro-nitroso-methane tetrafluoroethylene)	70-80	7	D	20				174% volume swell, poor elastomeric properties, different oven cures reduce swell to 48% but retain poor elastomeric properties	
Viton A	55-60	30	D	11				Dissolved	
Viton B (Stillman Ex 774M-1)	63-67	30	D	4				181% volume swell	
Parker V494-7	63-67	30	D	4				292% volume swell	

a -- Definitions of ratings are given on page 4-14.

TABLE 5.2 (CONT)
COMPATIBILITY OF NONMETALS WITH N₂O₄

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE					
		LIQUID		VAPOR		REMARKS	
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE
FLUORO RUBBERS (CONT)							
Formulas 75-79, 84, 85 and 94-99	70-80	7	D	20, 24			Fluoro rubbers with added fillers did not reduce volume swell below 190%, poor to good strength retention
Kel-F 3700, 5500	55-65		D	15, 19			> 300% volume swell in 45 minutes
Stillman TH 1057	55-65	31	D	19			205% volume swell
FLUORO SILICONE RUBBERS							
LS 53	63-67	30	D	4, 15, 20			> 200% volume swell
Formulas 55-67 and 80-83	70-80	7	D	20, 24			Fluorosilicone rubbers with added fillers did not reduce volume swell below 120%
LS-63	63-67	30	D	4			172% volume swell
Hadbar Series 58789-23	70-80	7	D	1			> 185% volume swell
58789-23GT	63-67	30	D	4			145% volume swell
MISCELLANEOUS RUBBERS							
Buna N	55-60	-	D	15			
Neoprene	55-60	-	D	15			

a — Definitions of ratings are given on page 4-14.

TABLE 5.2 (CONT)

COMPATIBILITY OF NONMETALS WITH N₂O₄

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE						REMARKS	
		TIME IN DAYS		LIQUID		VAPOR			
		RATING ^a	REFERENCE	RATING ^a	REFERENCE	RATING ^a	REFERENCE		
MISCELLANEOUS RUBBERS (CONT)									
Hypalon	55-60	-	D	15					
Cohriastic 500 (Silicone)	55-60	-	D	15					
Silicone O-ring with Kel-F Cover	55-65	63	D	19				Core shredded	
LUBRICANTS									
DC 11	63-67	14	C	4	14	C	4	Washed off in liquid, partly in vapor	
DC Hi Vac	63-67	14	C	4	14	C	4	Washed off in liquid, partly in vapor	
	55-60	30	D	11				Dissolved	
Rayco -30 Grease	55-60	30	D	11				Decomposed	
Kel-F 90	55-60	30	D	11				Dissolved	
Polyglycol Oils	63-67	14	D	4				Reaction	
L-1111-oil	63-67	14	C	4				2 - Phase layer washed off	
Molykote Z	55-60	30	A	11				Satisfactory	
Drilube 703	55-60	30	A	11				Satisfactory	
Electrofilm 66-C	55-60	30	A	11				Satisfactory	
TMSF-1,2,3	55-60	30	D	11				Crystallized	
QC-2-0093	55-60	30	D	11				Broken up	
QC-2-0026 Dow									

a - Definitions of ratings are given on page 4-14.

TABLE 5.2 (CONT)
COMPATIBILITY OF NONMETALS WITH N₂O₄

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE						REMARKS	
		LIQUID		VAPOR		TIME IN DAYS REFERENCE	TIME IN DAYS REFERENCE		
		RATING ^a	REFERENCE	RATING ^a	REFERENCE				
<u>LUBRICANTS (CONT)</u>									
Rayco -32 Grease	55-60	30	D	11				Decomposed	
Halocarbon Grease	63-67	14	C	4	14	C	4	Washed off in liquid, partly in vapor	
Nordoseal 147 and 421	70-80	-	C	4,19				Used satisfactorily for hardware assembly	
<u>THREAD SEALANTS</u>									
N ₂ O ₄ sealant	70-80	30	A	1				Satisfactory	
	160	7	A	1				Satisfactory	
Roddy Lube 100	63-67	14	A	4	14	A	4	Satisfactory	
200	63-67	14	A	4	14	A	4	Satisfactory	
Waterglass Graphite	63-67	14	A	4	14	A	4	Satisfactory	
Vydex A	63-67	14	C	4	14	C	4	Partially washed off	
<u>ADHESIVES</u>									
Armstrong A-6	55-60	30	D	11				Fell apart	
EC 847	55-60	30	D	11				Fell apart	
HT 424	55-60	30	D	11				Fell apart	
<u>CERAMICS</u>									
Temporell 1500	55-60	30	C	11				Slight precipitate	

a — Definitions of ratings are given on page 4-14.

TABLE 5.2 (CONT)
COMPATIBILITY OF NONMETALS WITH N_2O_4

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE						REMARKS	
		LIQUID			VAPOR				
		TIME IN DAYS	RATING ^a	REFERENCE	TIME IN DAYS	RATING ^a	REFERENCE		
CERAMICS (CONT)									
Sauereisen P-1	55-60	30	A	11				Satisfactory	
Sauereisen 31	55-60	30	C	11				Slight precipitate	
Sauereisen 47	75	-	D	4				Dissolved within 10 minutes	
Rockflux	75	-	C	4				N_2O_4 was absorbed, slight lifting from concrete	
PAINTS									
Epoxy No. 1	55-60	30	D	11				Dissolved	
Modified Epoxy No. 5	55-60	30	D	11				Dissolved	
Epoxy No. 7	55-60	30	D	11				Dissolved	
Epoxy No. 9	55-60	30	D	11				Stripped off	
Epoxy 6809	55-60	30	D	11				Dissolved	
Alkyd No. 4	55-60	30	D	11				Dissolved	
Polyurethane	55-60	30	D	11				Stripped	
Catalac									
Primer and Finished on Mild Steel	63-67	10	D	4				Paint lifted within minutes	
Improved	63-67	-	D	4				Paint lifted, and blistered within 2 minutes	
Acrylic Nitro-Cellu- lose	55-60	30	D	11				Dissolved	
Vinyl	55-60	30	D	11				Blistered	

a — Definitions of ratings are given on page 4-14.

TABLE 5.2 (CONT)
COMPATIBILITY OF NONMETALS WITH N₂O₄

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE					
		TIME IN DAYS			TIME IN DAYS		
		RATING ^a	REFERENCE	RATING ^a	REFERENCE	REMARKS	
<u>PAINTS (CONT)</u>							
Primer MIL-P-6880	50-60	30	D	11			Stripped off
Tygon A	75	-	D	4			Blistered within 30 minutes
Co-Polymer P-3000	75	-	D	4			Dissolved in 3 minutes
CA 9747 Primer	75	-	D	4			Reacted and dissolved within 3 minutes
Corrosite Clear 581	75	-	D	4			Blistered within 30 minutes
<u>POTTING COMPOUNDS</u>							
PR 1421	50-60	30	D	11			Dissolved
KIV 30	55-60	30	D	11			Dissolved
Epon 828	55-60	30	D	11			Dissolved
Parapine P-43	55-60	30	D	11			Dissolved
Proseal 793	55-60	30	D	11			Dissolved
Fairprene 5150	55-60	30	D	11			Partially dissolved
Crystal M & CF	55-60	30	C	11			Limited use only

a -- Definitions of ratings are given on page 4-14.

TABLE 5.2 (CONT)
COMPATIBILITY OF NONMETALS WITH N₂O₄

MATERIAL	TEMPERATURE DEGREES FAHRENHEIT	STATIC EXPOSURE				REMARKS
		TIME IN DAYS RATING ^a	REFERENCE	TIME IN DAYS RATING ^a	REFERENCE	
<u>MISCELLANEOUS</u>						
Johns Manville No. 50	55-65	7	D 19			Balts formed
Graphitar No. 2	55-65	30	A 19			
No. 50	55-65	30	A 19			
Garilock 900	55-60	30	D 11,19			Sample delaminated

a - Definitions of ratings are given on page 4-14.

5.3 EFFECTS OF N₂O₄ ON MATERIALS OF CONSTRUCTION

Table 5.3 mentions materials frequently used for construction. Included are the compatibility results of short exposures to N₂O₄ vapors and to watered N₂O₄. Reference 4 gives the details of these tests in which coatings and/or surface treatments were applied to various materials to ascertain resistance to N₂O₄ spills. Of the organic coatings, none exhibit sufficient resistance to N₂O₄. Water glass protects concrete from N₂O₄ and from nitric acid which is formed when N₂O₄ combines with water.

TABLE 5.3

COMPATIBILITY OF CONSTRUCTION MATERIALS WITH N₂O₄

Material	Temperature (°F)	Exposure Time	Remarks
Birch Wood	75	30 min	Surface darkened; attacked at H ₂ O-N ₂ O ₄ interface
Concrete			
Bare	75	1 hr 42 min	Concrete attacked
Coated with water glass	75	1 hr	No apparent reaction; affords protection
Coated with water glass and floor enamel (Esco Brand 41138)	75	30 min	Reaction at H ₂ O-N ₂ O ₄ interface after 6 minutes; stripped to water glass
Coated with water glass and Chex-Wear floor enamel	75	3 min	Only paint removed
Coated with Rockflux	75	1 hr 15 min	N ₂ O ₄ absorbed; adhesion weakened; material turned white
Mild Steel Coated with			
Tygon K paint	75	20 min	Paint blistered
Catalac, improved	75	10 min	Paint blistered; lifted when totally immersed
Co-Polymer P-200G	75	2 min	Dissolved immediately
Sauereisen 47 (4 coatings)	75	10 min	Dissolved
CA9747 Primer Paint	75	2 min	Reaction and discolored immediately
Corrosite Clear 581	75	30 min	Blistered

5.4 EFFECTS OF CONTAMINANTS ON N_2O_4

Traces of type 347 SS, 6061 aluminum alloy, and lint may be found as contaminants during missile systems manufacturing. To determine the effects of such contaminants on N_2O_4 , quantities of lint and shavings of type 347 SS and 6061 aluminum alloy were exposed to N_2O_4 at 70°F for seven days. No severe pressure build-ups were encountered during these tests and the N_2O_4 composition was unchanged (Reference 19). Water is a serious contaminant since it combines with N_2O_4 to form dilute nitric acid which exhibits more-corrosive properties than N_2O_4 . Also, the presence of organic compound, such as alcohols, acetones, and gasoline, are undesirable contaminants because of their reactivity with N_2O_4 .

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SECTION 6.0

PROPELLANT HANDLING

SECTION 6.0

PROPELLANT HANDLING

6.1 FIRE FIGHTING

The 50/50 fuel blend is flammable in both liquid and vapor states. Since the vapor over the fuel blend at 72°F is predominantly UDMH (Reference 3), the flammability hazards of the mixture are the same as for UDMH. Based upon the lower limit of flammability of UDMH, 2.3 volume percent in air at one atmosphere and 5°F (Reference 23), the fuel blend vapors are flammable in air in concentrations from 2.3 to 100 volume percent. Thus, mixtures within these limits can be ignited by electric spark, hot wire, or open flame.

Large quantities of water should be used to extinguish fuel blend fires. Based upon the flash and fire point data reported in Section 2.0 of this handbook, a dilution of three volumes of water to two volumes of the fuel blend is required to increase the flash and fire point temperature in air to 160°F.

Atlantic Research Corporation (Reference 25) has ignited liquid N₂H₄ and UDMH at 80°F with a jet of N₂O₄ vapor. Similar tests were conducted with each fuel diluted with water until no ignition occurred. No ignition occurred when the N₂H₄ was less than 60 volume percent and when the UDMH was less than 70 volume percent. Based upon these tests and the flash and fire points data given in Section 2.0 of this handbook, all fuel blend spills at 80°F should be diluted with water to a concentration less than 60 volume percent. This dilution will preclude fires caused by electric spark, hot wire, open flame, or N₂O₄ vapors.

Atlantic Research Corporation also reported that water sprays directed at fuel fires supported by air or by N₂O₄ vapors are more effective extinguishing agents than foams.

Nitrogen tetroxide is a stable, nonflammable, shock-insensitive compound. Alone, N₂O₄ will not burn, but its vapors will support combustion. If fire supported by N₂O₄ occurs, shut off the N₂O₄ supply and use an extinguisher that is compatible with the burning material.

The explosivity of the liquid phase reaction between the 50/50 fuel blend and N₂O₄ is discussed under Flammability and Explosivity, Section 8.0 of this handbook.

6.2 FUEL MIXING

As mentioned under Physical Properties of 50/50 Fuel Blend, Section 2.0 of this handbook, UDMH and N_2H_4 are miscible in all proportions. However, because their densities differ, they are easily layered, UDMH above the N_2H_4 .

With sufficient agitation, the N_2H_4 and UDMH are readily mixed so that the smallest unit volume of the mixture contains as many molecules of each component as every other unit volume. Upon attaining this state of mixing, there is no tendency whatever for the compounds to separate provided that the more-volatile UDMH is not permitted to evaporate from the vessel. The same forces that cause the layered components to mix will assure the permanence of the completely blended mixture. This does not mean that N_2H_4 and UDMH cannot be separated, but separation can be accomplished only by the transfer of energy in certain types of physical processes (fractional distillation) and chemical processes (formation of chemical derivatives) (Reference 1).

Under conditions where only partial mixing has occurred, strata of different compositions and densities can exist. Gravity will cause these strata to rise and fall in relation to each other. However, this phenomenon cannot be interpreted as a separation of the compounds because complete mixing was never attained. Thus, any condition short of complete blending cannot be tolerated and the measures required to effect complete blending must not be neglected (Reference 1).

When N_2H_4 and UDMH are mixed, small bubbles of dissolved gas are formed, there is a decrease in temperature, and the mixture occupies a smaller volume than the original combined volume of both. The shrinkage in volume is partly due to the drop in temperature; however, freshly mixed fuel blend that is allowed to warm to the temperature of the unmixed components still incurs a shrinkage of about 1.6%. The additional shrinkage is due to some form of loose bonding between the N_2H_4 and UDMH molecules which results in a more-compact molecular arrangement when the two are mixed (Reference 1).

Quantities of fuel were mixed using various mixing techniques as discussed in the following paragraphs.

6.2.1 Mixing by Agitation

Approximately 35 gallons of the fuel blend were mixed by adding N_2H_4 to UDMH in a type 304 SS 55-gallon drum (Reference 2). Mixing was accomplished by first rolling the drum on its side then end over end for 15 minutes.

6.2.2 Mixing by Diffusion

Approximately one pint of N_2H_4 was added to an equal amount of UDMH in a glass container. The fuel mixture remained undisturbed except for sampling. After 50 days, a homo-

geneous mixture through diffusion was obtained (Reference 4). This method is not recommended for use because of the time element and the uncertainty of its effectiveness when blending large quantities.

6.2.3 Mixing by Mechanical Stirring

Approximately one quart of fuel blend was mixed in a glass container. Mixing was accomplished in a nitrogen atmosphere with a glass stirrer turning at 760 rpm for five minutes and 1 rpm for 72 hours. The ratio of the area of the stirrer (2.5 in.²) to the volume (48.7 in.³) of the blend was 0.05. If this technique is feasible for large-scale mixing, it can be used with success.

6.2.4 Mixing by Gas Bubbling

Approximately one quart of fuel blend was mixed successfully with a nitrogen gas stream. This method is not recommended because UDMH losses are incurred during the operation (Reference 4).

6.2.5 Mixing by Impingement

A mixing chamber similar to that described by W. R. Ruby (Reference 26) was used to mix laboratory quantities of the fuel blend. Photographs of the apparatus and a detailed procedure is presented in Reference 4. Mixing was accomplished when two streams of UDMH impinged tangentially with two streams of N₂H₄.

Wyle Laboratories (Reference 37) successfully mixed approximately 41,000 pounds (110 drums) of the fuel blend by recirculating the fuels through a blender (which caused mixing similar to the impingement technique) and into a storage tank. Following the initial transfer of each fuel into the storage tank, two centrifugal pumps provided continuous circulation through the blender for approximately two hours before mixing was accomplished.

Aerojet-General Corporation (Reference 1) also has blended thousands of gallons of the fuel blend by pumping the fuel components simultaneously from each tank into a concentric nozzle containing a swirling mechanism to enhance mixing, and then into the fuel blend storage tank.

6.3 FREEZE AND THAW OF 50/50 FUEL BLEND

A laboratory test was conducted to determine the effect of alternate freezing and thawing of the fuel blend. The apparatus used, a description of the test procedure, and the detailed test results are presented in Reference 2. Results of these tests indicate that the fuel blend separates when subjected to freezing and thawing conditions. When freezing occurs, the N₂H₄ solidifies

first because its freezing point is 55°F. The solid N₂H₄ particles tend to fall to the bottom because they are more dense than UDMH. Since analyses indicate that separation occurs, fuel blend subjected to freezing point temperature should be re-mixed prior to use.

6.4 STORAGE

Fuel blend was stored for six months at 60° ± 5°F in a two-quart 1100 aluminum alloy tank and a one-quart Pyrex glass bottle. No fuel decomposition was detected in either container (Reference 4).

Spectral analyses of the fuel blend in a one-quart Pyrex glass bottle gave no evidence of fuel blend separation after three months (Reference 4).

The fuel blend was stored in sealed Pyrex glass ampules at 200°F for 12 weeks (References 2 and 4). Employing the weight loss technique for measuring fuel decomposition resulted in inconclusive data. However, spectral analyses and visual examination of the fuel indicated no significant change after the storage period. Also, no positive pressure was detected when each ampule was opened. These observations indicate no decomposition.

Low-temperature and high-temperature storage tests were conducted with N₂O₄. Allied Chemical Corporation reports that N₂O₄ was stored out-of-doors in a small carbon steel container for nine years at temperatures ranging from 68° to 100°F. Post-test analyses showed no change in propellant composition.

In another test, N₂O₄ was stored in 10-gallon tanks made from PH 15-7 Mo stainless steel and 6061-T6 aluminum alloy for six months at temperatures ranging from 0° to 100°F. Chemical analyses after the test showed no change in propellant composition and a visual examination of the interior of the tank indicated no metal attack (Reference 19).

For three months, N₂O₄ was stored at 270° ± 10°F in two-quart tanks made from PH 15-7 Mo and 347 SS and from 6061-T6 aluminum alloy. The N₂O₄ remained unchanged except for a trace of nitric acid found by spectral means and an indication of the entry of water. Visual examination of the tanks disclosed salt deposits.

In the foregoing high-temperature storage tests, moisture was prevented from entering the system to preclude the formation of nitric acid from the N₂O₄. The acid in turn would have reacted with the stainless steel and aluminum alloy to form nitrates that are insoluble in N₂O₄.

Because titanium tends to react with oxidizers such as RFNA (Reference 27) and fluorine (Reference 28) to form unstable compounds which violently decompose, a one-month storage test of N₂O₄ in a titanium tank (C120AV) was conducted at cycling temperatures between 90° and 150°F (Reference 19). No abnormal pressures were detected during the test period; at the con-

clusion of the test, a 50-pound weight was dropped from a height of two feet onto the tank to determine if shock-sensitive deposits had formed. No reaction to this shock was observed. The chemical composition of the N₂O₄ remained unchanged and examination of the tank interior showed no signs of deposits.

6.5 CLEANING AND FLUSHING

Field experience with missile systems indicates that components such as valves, flow regulators, lines, fittings, and filters which have been serviced and/or used with propellants should be decontaminated prior to being set aside for down-time or storage periods.

Bell Aerosystems evaluated various flush procedures for 90 days storage using RASCAL thrust chamber bipropellant valves (Reference 4). A cross-section of the valve and a list of the flush procedures are given in Reference 2. The best flush procedure for the oxidizer system proved to be a tri-liquid flush and, for the fuel system, an alcohol flush.

The tri-liquid flush procedure involves water inhibited with chromium trioxide, methanol, and methylene chloride. The water dissolves any metal nitrate salts and removes excess N₂O₄; the methanol combines with the water and with continuous cycling replaces the water; and the methylene chloride combines with residual methanol. The final purge with warm nitrogen easily vaporizes the low-boiling methylene chloride.

For the fuel system, an isopropanol or methanol flush procedure is recommended. The fuel blend is soluble in either of these alcohols. Briefly, the flush procedure is as follows:

- (1) Drain the propellants and purge the valve with nitrogen gas.
- (2) Flush the oxidizer system with inhibited water, cycling the valve ten times (15 seconds open and 15 seconds closed).
- (3) Flush the fuel system with isopropanol or methanol, cycling the valve ten times (15 seconds open and 15 seconds closed).
- (4) Flush the oxidizer system with methanol, cycling the valve ten times (15 seconds open and 15 seconds closed).
- (5) Flush the oxidizer system with methylene chloride, cycling the valve ten times (15 seconds open and 15 seconds closed).
- (6) Purge the oxidizer and fuel systems dry with warm nitrogen (140° to 160° F), cycling the valve ten times (15 seconds open and 15 seconds closed).

The cycling time may be extended, depending upon the complexity of the systems.

Aerojet-General Corporation (Reference 1) is evaluating a liquid flush procedure for flight test engines. Triethanolamine solutions with various additives are being used to neutralize residual oxidizer and hydroxyacetic acid solution, and various additives are being used to neutralize the residual fuel. The flush procedure they used after acceptance testing is as follows:

- (1) Drain propellants.
- (2) Open thrust chamber valves and place plug in nozzle of the thrust chamber.
- (3) Fill and drain fuel and oxidizer systems simultaneously with water.
- (4) Fill and drain oxidizer system three times with alkaline (triethanolamine) neutralizing solution.
- (5) Fill and drain fuel system three times with acid (hydroxyacetic) neutralizing solution.
- (6) Fill and drain fuel and oxidizer systems simultaneously with water.
- (7) Fill and drain fuel and oxidizer systems simultaneously with alcohol for drying.
- (8) Purge fuel and oxidizer systems dry with hot nitrogen gas.

Several pickling and degreasing procedures were applied to type 316 SS and 2014-T6 aluminum alloy coupons that were partly immersed in the 50/50 fuel blend at 160°F for about two months. Some of the aluminum alloy coupons were welded. These tests were conducted to determine whether or not certain degreasers and/or pickling solutions would result in severe discoloring of the metal coupons or the fuel blend (reference 4).

Three pickling procedures and three degreasers were applied to 2014-T6 coupons. The pickling procedures used are described in Reference 4. The degreasers used were trichlorethylene, trichlorethane, and Arseco (a safety solvent principally containing kerosene). Each test coupon exhibited good corrosion and was assigned an "A" rating. The fuel blend was unaffected and only slight staining was detected on the surface of the coupon.

Type 316 SS welded and unwelded coupons were acid-pickled and then degreased with trichlorethylene, trichlorethane and Arseco. The pickling procedure used is described in Reference 4. Again, the fuel blend was unaffected and the corrosion rates merited an "A" rating. Slight staining was observed in the vapor phase.

SECTION 7.0

SAFETY

SECTION 7.0

SAFETY

7.1 NOMINAL 50/50 FUEL BLEND

7.1.1 Health Hazards

Generally it is suggested that any handling mishaps or similar situations be treated as though caused by UDMH or N_2H_4 alone, depending upon which of the two fuels causes the more serious effects.

Arthur D. Little, Inc. has reported on fuel blend toxicity (Reference 29). Animal experiments conducted at ADL failed to show significant synergistic effects caused by the combined toxicity of UDMH and N_2H_4 . The M.A.C.^a value for N_2H_4 is 1 ppm and for UDMH it is 0.5 ppm. ADL graphically illustrated that when the vapor is contaminated with 0.25 ppm UDMH, the maximum allowable N_2H_4 is 0.5 ppm (see Figure 7.1). Regarding short-term exposure, Dr. Leslie Silverman of the Harvard Medical School of Public Health has suggested that the M.A.C. value can be exceeded safely by a factor of ten with the 60/60 rule menu for a 10-minute period. Dr. E. C. Wortz (Reference 35) of The Marin Company has calculated data to show that the M.A.C. value can be exceeded by a factor of five for each fuel separately. Dr. Wortz's data is considered as safe short-term exposure limits.

Studies of the effects from repeated exposure of rodents and dogs to UDMH vapor were conducted at the Army Chemical Center (Reference 42) to obtain data for estimating the quantity of toxicant to which man may be exposed without harmful effects. Based upon the results of these experiments, the M.A.C. of UDMH vapor for man should be well below 5 ppm. Until more data and experience are available, 0.5 ppm should be used as a guide to good industrial handling and safe practice.

Experience with human exposure to N_2H_4 and UDMH is limited, but cases of delayed and possibly cumulative conjunctivitis have been reported among men in plants manufacturing N_2H_4 . These employees complained of nausea, dizziness, and headache. The occurrence of dermatitis also was reported.

a—Maximum Allowable Concentration. These represent values to which man can be exposed for a normal working day, day after day, without adverse effects upon his health.

<u>PROPELLANT</u>	<u>M.A.C.(ppm)</u>
UDMH	0.5
N_2H_4	1.0

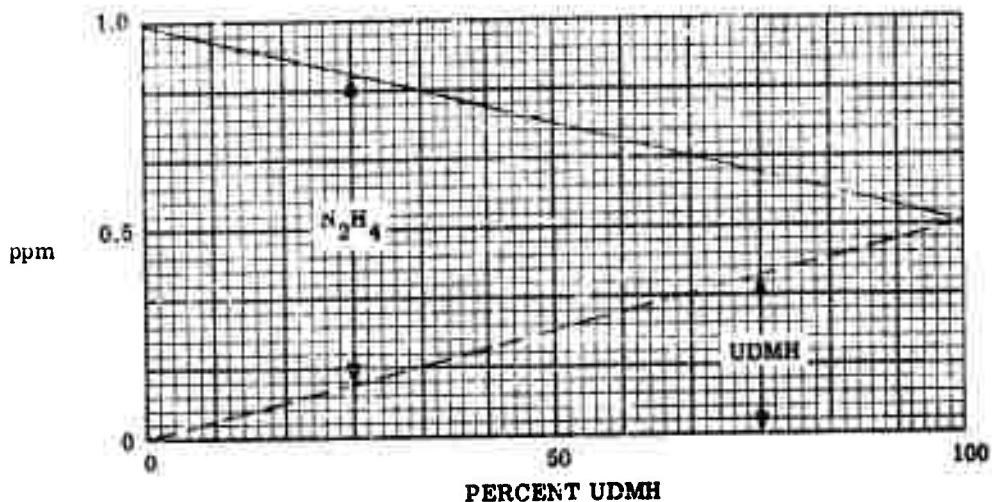


Figure 7.1. Combined Tolerable Vapor Contamination

In sufficient amounts, UDMH is toxic by inhalation, ingestion, and skin contact producing several significant systemic effects. In addition, it produces local irritating effects upon the eyes and the respiratory tract; UDMH has little or no local effect on the skin, but is readily absorbed into the body by this route.

7.1.2 Protective Clothing

Personnel handling the fuel blend should wear protective clothing. In general, rubber suits, boots and gloves, and hoods will suffice. The recommended protective clothing is:

- (1) Boots and gloves - GRS rubber.
- (2) Gloves, vinyl-coated, type R-1, under specification MIL-G-4244 (Reference 30).
- (3) Gloves, Blulettes, DuPont neoprene rubber, Pioneer Rubber Company, Willard, Ohio.
- (4) Gloves, Edmont, Cadet style, 7897, Edmont Inc., Coshocton, Ohio.
- (5) Suit, vinyl-coated fiberglass, inner type MA-1, MIL-S-4553 (USAF) (Reference 30).
- (6) Suit, MIL-S-12527 (QMC) (Reference 30).
- (7) Polyethylene clothing may be used (Reference 30).
- (8) Fiberglass clothing impregnated with Teflon or Kel-F (Reference 30).

When entering an area where a high concentration of fuel blend vapor is present, a self-contained air source such as a Scott Air-Pack should be worn. A canister-type protective breathing apparatus is effective up to 30 minutes for contamination levels up to 10,000 ppm (Reference 29).

Large quantities of the fuel blend should be transferred in clean, closed metal systems. The fuel blend should be blanketed with nitrogen at all times.

7.1.3 First Aid

Skin areas splashed with the fuel blend should be washed copiously with water. The eye, if contaminated, should be flushed copiously and thoroughly with water.

Personnel suspected of inhaling fuel vapor poison should leave the contaminated area and breathe deeply of fresh air. If fuel is taken internally, induce vomiting. Individuals over-exposed should be examined by a physician; regular handlers should be examined by a physician periodically.

7.1.4 Disposal

Leaks or spills of fuel blend should be dealt with only by personnel wearing adequate protective equipment. Dilution with minimum quantities of water, flushing down drains into catch basins, should be accomplished as soon as possible. Minimum quantities of water are recommended so that the diluted fuel eventually may be disposed of by burning.

During testing at Bell under another program, an undetected UDMH spill drained into a nearby waterway. Shortly thereafter, dead fish were seen floating on the surface of the water. State water pollution authorities attributed the dead fish to UDMH which eventually led to extensive testing by the Water Pollution Control Board and the U. S. Public Health Service. These tests revealed that one ppm of UDMH and/or N_2H_4 had an adverse effect upon fish (Reference 31). Because of this, steps were taken at Bell to destroy UDMH and/or N_2H_4 . Subsequently, calcium hypochlorite^a was used for the chemical destruction of small quantities of UDMH and N_2H_4 prior to draining into a public waterway.

Because the fuel blend in water can have adverse effects on fish and animals, it should not be added deliberately to drainage ditches or ponds. Bulk quantities should be collected in suitable containers for burning. When the fuel blend enters drainage systems by accident, it must be reduced to safe limits by addition of a chemical such as calcium hypochlorite which will decompose the blend (Reference 32).

a - Calcium Hypochlorite Needed: 1.6 lb/gal of solution containing 1% by weight N_2H_4 ; 0.8 lb/gal of solution containing 1% by weight UDMH.

R. W. Drake of The Martin Company has prepared a procedure for fuel blend disposal. When a water solution contains 1% or less fuel blend, calcium hypochlorite is used to destroy the fuel chemically; fuel concentrations in the range of 1% to 40% are burned in a furnace; fuel concentrations greater than 40% are burned in air.

7.1.5 Detection Devices

A portable detection kit for fuel, manufactured by the Mine Safety Appliance Company of Pittsburgh, uses a colorimetric test specific for UDMH. This device can measure quantities of UDMH in waste water and air samples (Reference 1). The range of this detector is 0 to 10 ppm.

Another device, manufactured by the American Systems, Inc., is reported capable of measuring small quantities of UDMH or N_2H_4 in the order of 0.25 ppm.

However, these devices have not been fully evaluated. One problem in particular concerns the effectiveness of the instruments when both fuel and oxidizer vapor come in contact with the sensing media simultaneously.

7.2 N_2O_4 OXIDIZER

7.2.1 Health Hazards

Dr. Tamas of the Aerospace Medical Division of WADD has indicated that, at vapor concentrations of 100 ppm or lower, N_2O_4 does not exist for purposes of practical measurement, but the vapors are primarily NO_2 . Even at concentrations as high as 10,000 ppm, only about 0.1% is N_2O_4 at room temperature and one atmosphere. Thus, as mentioned in the section on Detection Devices later in this handbook, instruments that are sensitive to NO_2 vapors are desirable.

Liquid N_2O_4 spillage on the skin or splashing in the eyes causes burns similar to those caused by 60% to 70% nitric acid. Brief contact of the liquid with the skin or other tissues results in yellow staining; if the contact is more than momentary, a severe chemical burn will result. The N_2O_4 vapors that contact the skin are less harmful than liquid contact for a comparable period of time. A stinging sensation results on the skin similar to that caused by nitric acid fumes. If splashed in the eyes, N_2O_4 can cause blindness. Taken internally, the burn can be sudden and severe, resulting in death (Reference 33).

Because of its toxic effects, inhalation of N_2O_4 vapors is normally the most serious hazard in the handling operations. The M.A.C. of this vapor is expressed as five parts of NO_2 per one million parts of air (2.5 ppm as N_2O_4) (Reference 34). Dr. Leslie Silverman (Reference 29) of the Harvard Medical School of Public Health has suggested that the M.A.C. value can be exceeded safely by a factor of five for a 10-minute period. Also, Dr. E. C. Wortz (Reference 35)

of The Martin Company has compiled data for short-term exposures to N_2O_4 ; for a 10-minute period, the M.A.C. value also may be exceeded by a factor of five. The Nitrogen Division of Allied Chemical (Reference 36) reports that a person was exposed to 158 ppm of NO_2 for 10 minutes without apparent effects; this value exceeds the M.A.C. by a factor of 30. Thus, Dr. Silverman's and Dr. Wortz's data appears to be safe values for short-term exposures.

7.2.2 Protective Clothing

Personnel handling N_2O_4 should wear protective clothing. Rubber suits, boots and gloves, and hoods will suffice. The protective clothing previously listed in the section on fuel blend safety is satisfactory for use with N_2O_4 . Personnel at Wyle Laboratories (Reference 37) while wearing two-piece protective suits developed nitric acid burns around exposed wrists and ankles. These burns resulted from nitric acid formation when NO_2 vapors and moisture came in contact with the skin. Recurrence of this was prevented by taping the jacket sleeves and pants cuffs to the wrists and ankles.

7.2.3 First Aid

When liquid or vapor N_2O_4 comes in contact with the skin, immediately wash with large quantities of water. When splashed into the eyes, flush the eyes with water continuously for 15 minutes, with a fellow employee assisting the injured by holding the eye open. Medical assistance should be summoned immediately. Administration of anything else, such as neutralizing agents, should be done only at the direction of a physician.

Persons exposed to excessive N_2O_4 fumes should be removed from the contaminated area immediately. The patient should be carried and not allowed to walk because exertion increases the effects of pulmonary edema. Administration of oxygen by trained personnel is desirable. Personnel exposed seriously should be removed to a hospital.

Swallowing of N_2O_4 should be treated by drinking large amounts of water (or milk, if available); medical attention should be summoned at once.

7.2.4 Disposal

Small and large quantities of N_2O_4 can be vented slowly out-of-doors through elevated stacks. Rocketdyne uses a 50-foot stack from 15,000-gallon tanks for venting when atmospheric conditions are favorable. The Nitrogen Division of Allied Chemical Corporation indicates that quantities of N_2O_4 can be drained or pumped into a pond where the N_2O_4 can be neutralized with soda ash, or allowed to boil off, provided that the area is not populated. Neutralization should take place prior to dumping into a waterway. Because water is only slightly soluble in N_2O_4 , and N_2O_4

is heavier, this process is time-consuming; the N_2O_4 might remain at the bottom and slowly convert to nitric acid. In addition, large quantities of N_2O_4 may be disposed of by burning with a fuel such as kerosene. Rocketdyne also burns N_2O_4 near test stand locations with liquid petroleum gas.

7.2.5 Detection Devices

There are several instruments available specifically for detecting the presence of oxides of nitrogen in air. The Kitagawa Company manufactures a portable detector for air sampling. A dry reagent turns yellowish brown at NO_2 concentrations of approximately 2.5 ppm. This instrument is distributed by the Union Industrial Equipment Corporation, Port Chester, New York (Reference 1). Mine Safety Appliance Company, Kruger Instrument Company, and American Systems Incorporated manufacture a recording device for detecting oxides of nitrogen in the order of 1 ppm. However, these devices have not been fully evaluated.

SECTION 8.0

FLAMMABILITY AND EXPLOSIVITY

SECTION 8.0

FLAMMABILITY AND EXPLOSIVITY

8.1 FLAMMABILITY

The introduction of hypergolic fuel-oxidant systems into the missile propulsion field has created many new problems. These problems arise in part from the hazards associated with the handling and storage of the fuel and oxidant in close proximity; accidental or premature contact of fuel and oxidant (liquid or vapor phase) can result in a sudden energy release. In an effort to understand the behavior of such systems under accidental spill conditions, the Bureau of Mines and Bell Aerosystems Company agreed to study the 50/50 fuel blend-N₂O₄ system. A detailed report is given in Reference 43. Briefly, four accident situations were considered:

- (1) Spillage of liquid fuel blend into N₂O₄-air atmospheres.
- (2) Spillage of liquid fuel blend onto a hot surface and subsequent contact of the vaporized fuel blend with N₂O₄-air atmospheres.
- (3) Contact of vapors leaking from a container of fuel blend with N₂O₄-air mixtures.
- (4) Passage of N₂O₄-air-fuel blend mixtures over an external ignition source.

Spillage of liquid fuel blend into N₂O₄-air mixtures was investigated over a range of temperatures by determining SIT at approximately one atmosphere in an apparatus described and discussed in Reference 3. The SIT is plotted versus N₂O₄ concentrations in air for liquid fuel blend, N₂H₄, and UDMH (Figure 8.1). The short horizontal lines on the curves in this figure represent the uncertainty of the N₂O₄ concentration measurement. In addition, the dew-point line for N₂O₄ is plotted (Reference 4).

The results given in Figure 8.1 show that the SIT of the fuel blend, N₂H₄, and UDMH differ little for N₂O₄ concentrations below 6%. Above 6% concentration, the SIT of the fuel blend is less than that of N₂H₄; above an N₂O₄ concentration of 9%, the SIT of the fuel blend is greater than that of UDMH. The double-valued nature of the SIT curves at the lower temperatures is due to the shift in N₂O₄ equilibrium with decreasing temperatures.

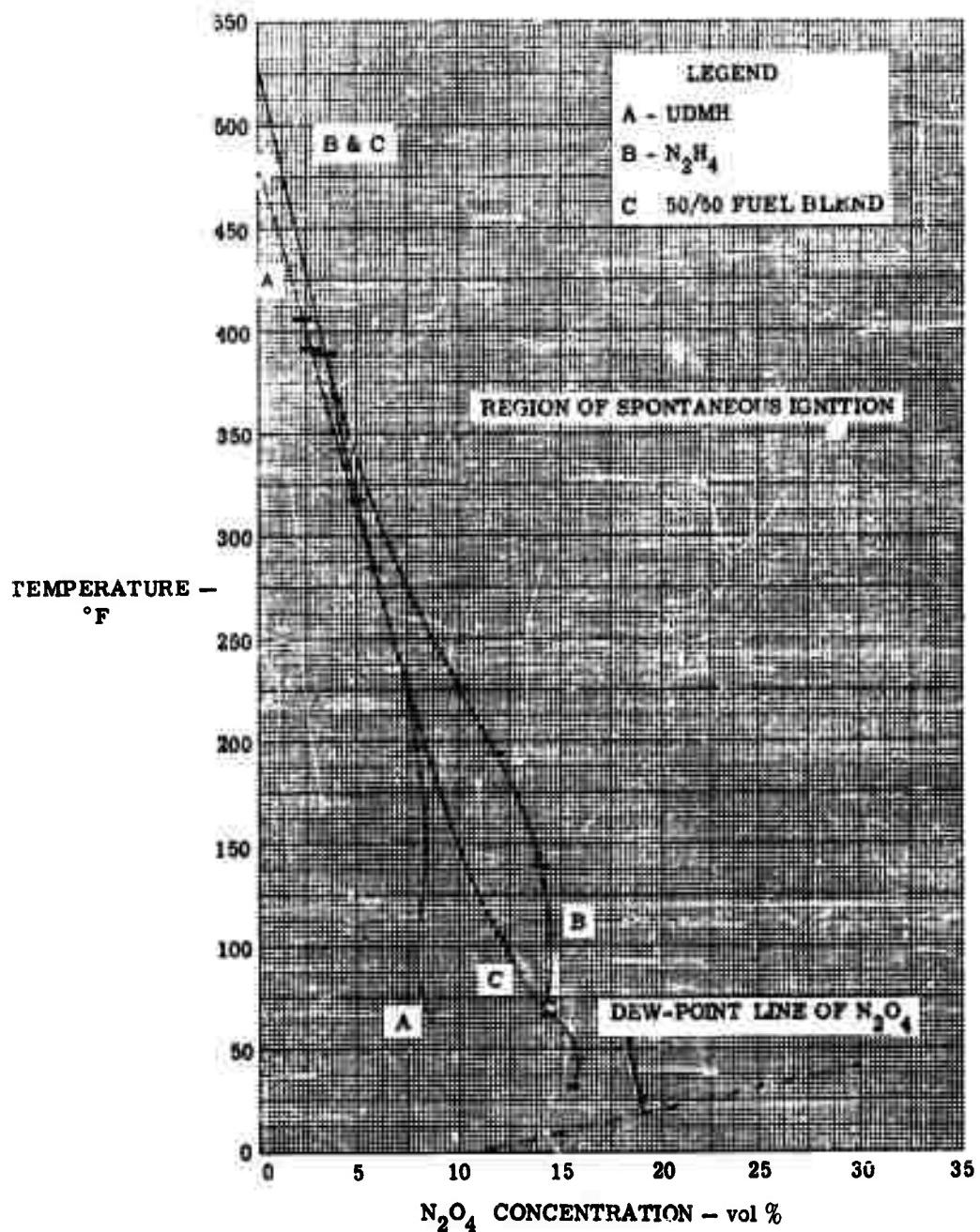


Figure 8.1. Spontaneous Ignition Temperatures of Liquid 50/50 Fuel Blend, N₂H₄, and UDMH in Contact with N₂O₄-Air Mixtures at 740 ±10 mm of Hg as a Function of N₂O₄ Concentration

Spillage of vaporized fuel blend into N₂O₄-air mixtures was investigated using the same apparatus. The tests were conducted by injecting N₂O₄-air mixture into an atmosphere of vaporized fuel blend-air mixture held at a specified temperature. Since vaporized fuel blend reacts with air, the residence time was held to one minute before injection of the N₂O₄-air mixture. The results shown in Figure 8.2 correspond to trials in which this residence time was used. The vertical arrows in the figure correspond to combustible concentrations below which ignitions were not obtained at temperatures up to 550°F.

Figure 8.3 shows a comparison between the SIT of vaporized fuel blend and UDMH in contact with 100% N₂O₄ vapors. The vertical dotted lines in Figure 8.3 represent the lower limits of flammability for each of the two combustibles in air at the maximum temperatures at which spontaneous ignition of each combustible air mixture was obtained in N₂O₄. The UDMH curve, unlike the fuel blend curve, extends to a combustible concentration equal to its lower limit of flammability in air at 360°F; the lower limit of flammability of the fuel blend is below the lower concentration limits at which spontaneous ignition occurs. This behavior may be due to the air oxidation of the N₂H₄ vapors in the vaporized fuel blend before the addition of N₂O₄.

Spontaneous ignition temperatures were determined for the equilibrium vapors of liquid fuel blend in contact with N₂O₄-air mixtures. Liquid fuel blend was evaporated at constant pressure from a vented container for a period of time sufficient to ensure vapor-liquid equilibrium. A mixture of N₂O₄ and air at room temperature (about 77°F) was injected into this vapor-air atmosphere and any ensuing reaction was noted. Sufficient liquid fuel blend was used to ensure that no appreciable change in its composition would occur. Results plotted in Figure 8.4 show the relation between the temperature of the equilibrium ignition and the composition of the N₂O₄-air mixtures which are injected into the hot vapors.

The vapors of N₂H₄ and UDMH from the fuel blend react in contact with N₂O₄ to produce a dense white cloud of fine particles, gaseous and solid. Such reactions were observed over a wide range of fuel concentrations at pressures as low as 2 mm of Hg. Because of this, flame propagation (flammability) tests conducted on N₂H₄ and UDMH in N₂O₄-air mixtures are, in reality, tests on the reaction products. The only combustibles found in the gaseous products were ammonia and hydrocarbons.

SECTION 8.0
50/50 FUEL BLEND
AND N_2O_4

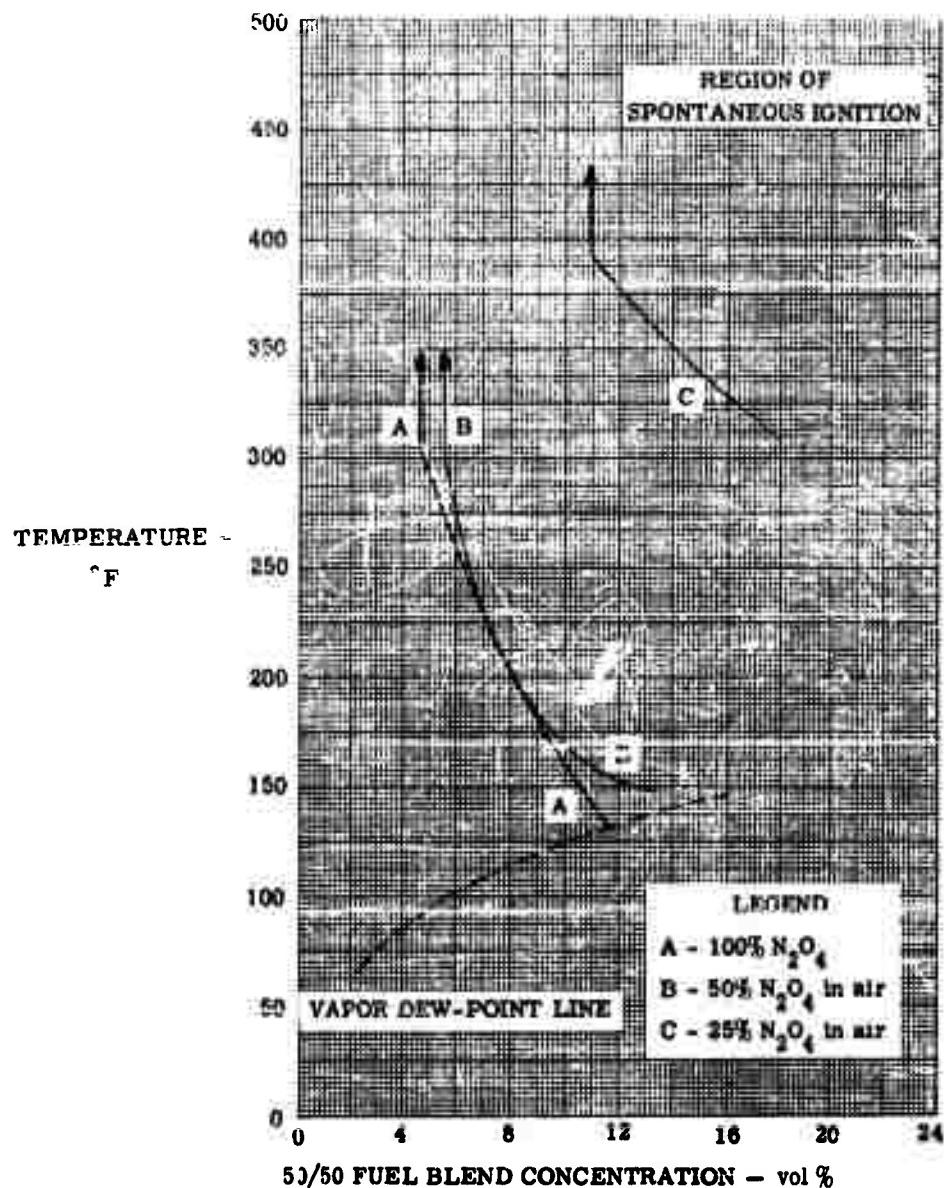


Figure 8.2. Spontaneous Ignition Temperatures of Vaporized Fuel Blend and Air Atmospheres in Contact with Various N_2O_4 -Air Atmospheres at 740 ± 10 mm of Hg for Residence Times of One Minute

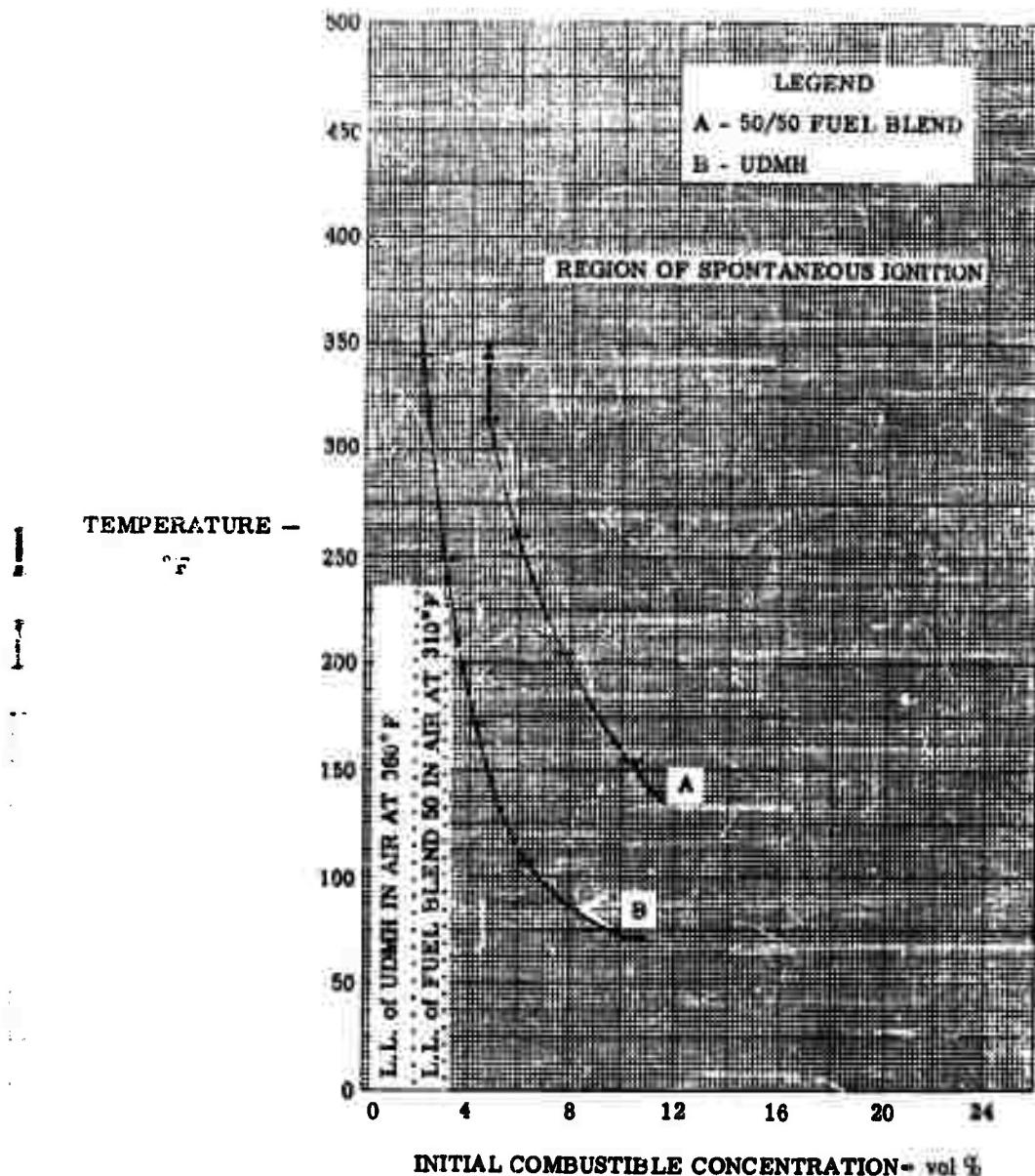


Figure 8.3. Spontaneous Ignition Temperatures of Vaporized (A) Fuel Blend-Air and (B) UDMH-Air Mixtures in Contact with 100% N₂O₄ at 740 ±10 mm of Hg as a Function of the Combustible Concentration in Air

SECTION 8.0
50/50 FUEL BLEND
AND N₂O₄

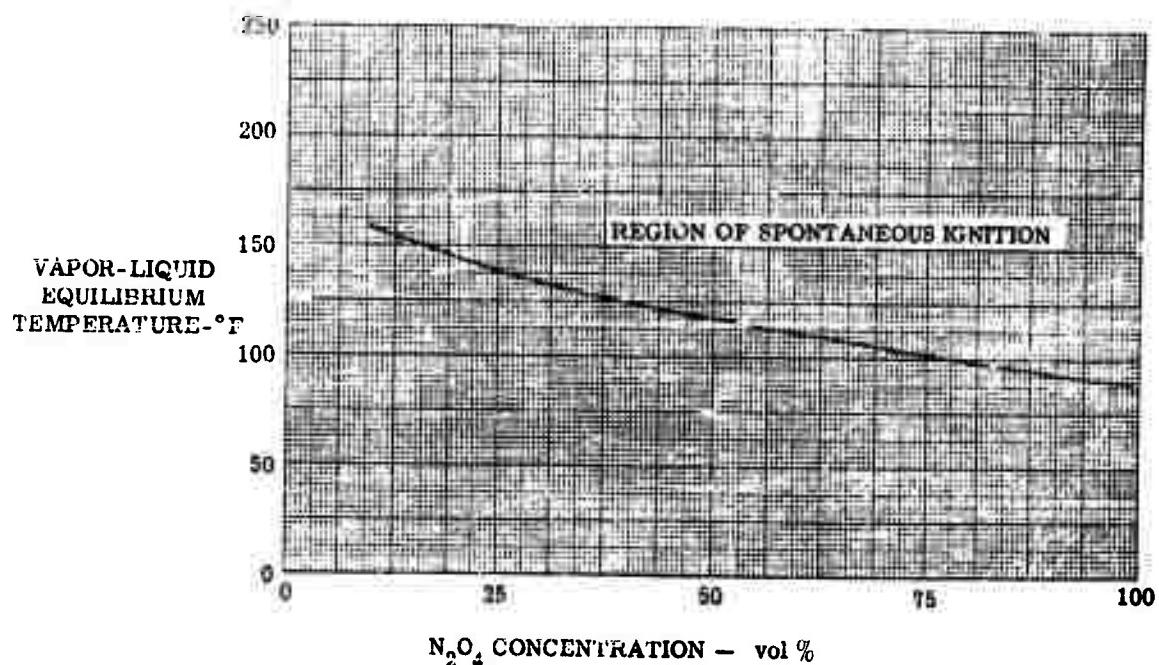


Figure 8.4. Vapor-Liquid Equilibrium Temperatures of Fuel Blend Required for Spontaneous Ignition of the Resulting Vapors in Contact with N₂O₄-Air Mixtures

In the absence of N₂O₄, the vapors of N₂H₄ and UDMH form flammable mixtures between 2.3 and 5.0 volume percent of the combustible vapor in air. The lower limits of flammability of N₂H₄-UDMH mixtures were calculated by using LeChateliers' Law (Reference 38). Results of these calculations are given in Figure 8.5 where the lower limit concentration of combustible vapor (N₂H₄ plus UDMH) is plotted as a function of the concentration of UDMH in the combustible. Because of the high dew point of N₂H₄, not all of the vapor-air mixtures represented by points on the curve in Figure 8.5 are physically possible at 77°F and one atmosphere of pressure. Note that the portion of the curve corresponding to impossible vapor-air mixtures is dotted. The vertical line in the figure represents a combustible vapor composition equal to that of the fuel blend. To determine the lower limit of flammability of a realistic vapor-air mixture from Figure 8.5, the vapor composition must be known. Accordingly, the pressure-composition diagram for mixtures of N₂H₄ and UDMH at 72°F was determined and plotted in Figure 8.6. The dotted line in this figure corresponds to the vapor pressure of the fuel blend at 72°F. The intersection of this dotted line with the vapor curve gives the composition of the equilibrium vapors over liquid fuel blend at 72°F (80 mole percent UDMH and 20 mole percent N₂H₄). From Figure 8.5, the lower limit of flammability for this vapor mixture in air at 77°F is 2.6 volume percent. However, the presence of N₂O₄ in the air tends to increase the measured value because the N₂H₄ and UDMH is converted to gaseous and solid products not all of which are combustibles.

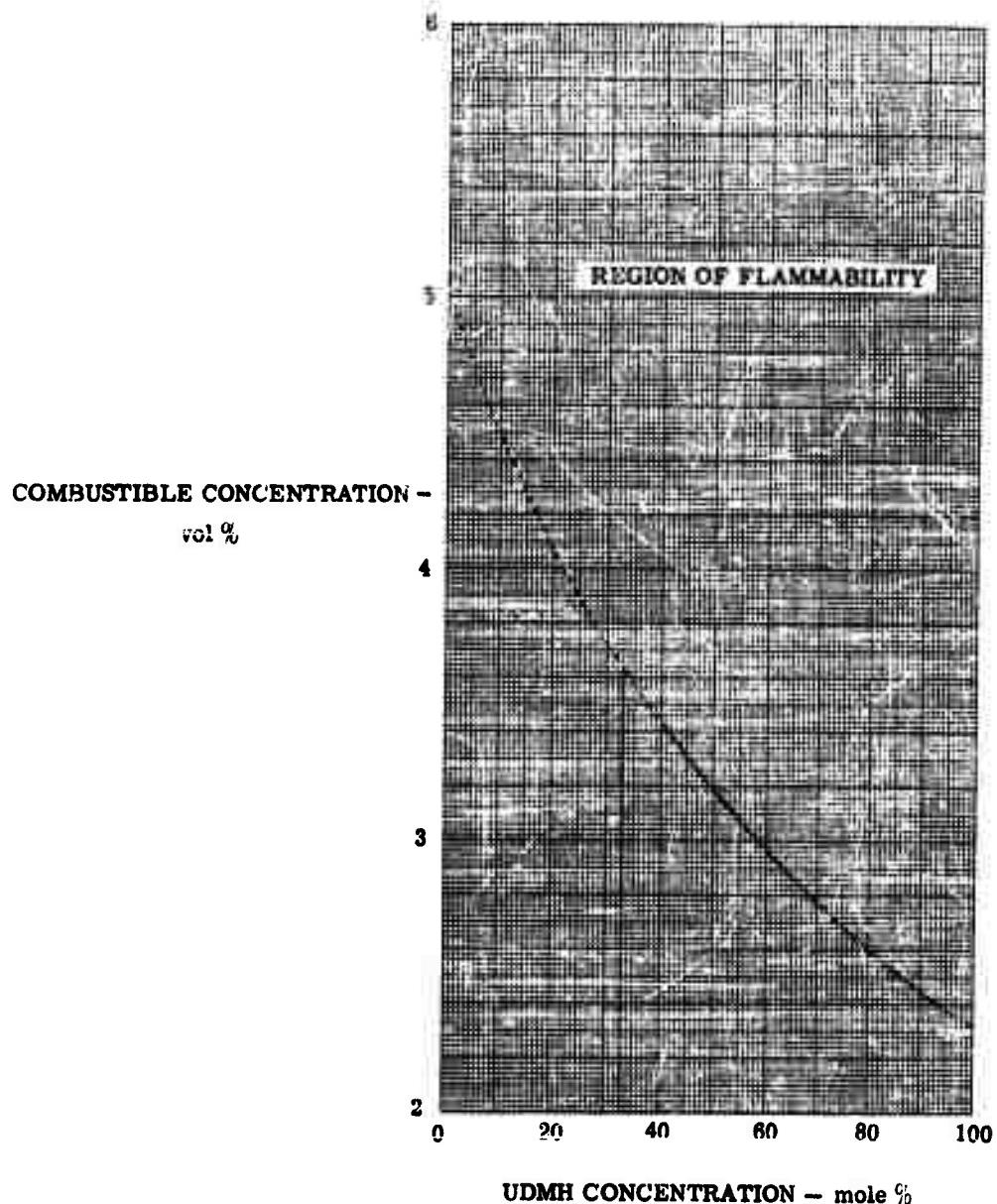


Figure 8.5. Lower Limit of Flammability of N₂H₄-UDMH Blend (Combustible) in Air at 77°F as a Function of UDMH Concentrations in Combustible

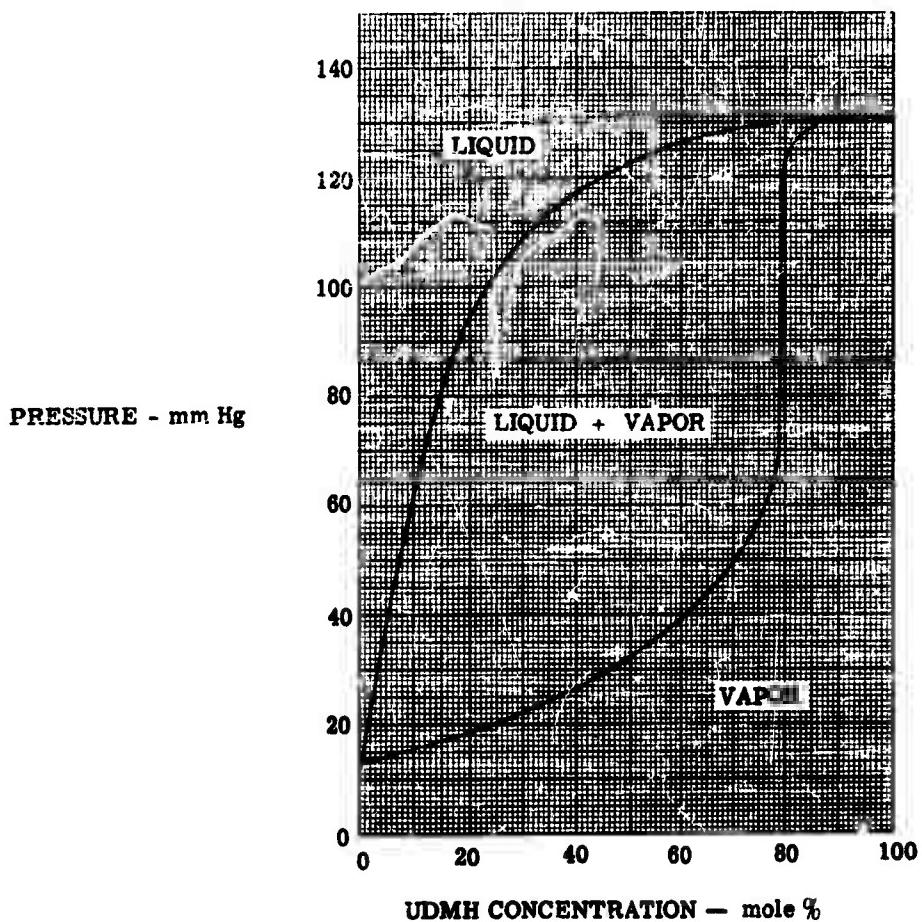


Figure 8.6. Pressure-Composition Diagram for the System N₂H₄-UDMH at 72°F

3.2 EXPLOSIVITY

Testing was conducted with laboratory quantities of N_2O_4 and the fuel blend 4) to determine whether or not propellant spills would lead to detonations. In Reference Penner distinguishes between explosions and detonations as follows. In an explosion the release rate and/or the number of molecules per unit volume increase with time more uniformly throughout a confined volume. A detonation wave, on the other hand, is spontaneous and is propagated through unreacted combustible mixtures by an advancing shock front. Exothermic chemical changes occur in such a way that the chemical heat released supports further propagation of the detonation wave.

A closed chamber, approximately 1/150-scale version of the actual Titan II was used for propellant spill tests (References 2 and 4). Spills were conducted with laboratory quantities of N_2O_4 and fuel blend at various mixture ratios with fuel leads and oxidizer leads. The last test involved combined propellants spilled into the chamber at a 2:1 mixture ratio was 0.1 pound. At this mixture ratio, when 0.066 pound (30 grams) of N_2O_4 was added to 0.033 pound of fuel blend, an explosion occurred damaging the test chamber.

Based upon these tests, the following facts are presented:

- (1) Spillage of these propellants may cause explosions, but not detonations.
- (2) An increase in propellant quantity increases the reaction violence.
- (3) For the most part, spills are more reactive when fuel is added to the oxidizer than when the oxidizer is added to the fuel at identical quantities and mixture ratios.

Multiple spill tests were performed by Rocketdyne (Reference 40) on the Titan II. Spills were conducted with 50 and 300 pounds of propellants in simulated Titan II configurations (1/10-scale and 1/18-scale versions). A 2-to-1 oxidizer-to-fuel ratio by weight was used. The following spill conditions were employed: simultaneous spills into a dry silo, simultaneous spills into water, fuel lead spill, and one simultaneous spill into water. Small-scale spills onto concrete also were conducted with 2.5 pounds of propellants. The data reported by Rocketdyne indicates that all explosions result from vapor phase reactions. In addition, the following was reported:

- (1) Silo spills with fuel leads were less severe than with either the simultaneous spills or the fuel lead conditions. The simultaneous spills resulted in the most violent explosions.
- (2) Increase in propellant weight increased the reaction violence on spills made under simultaneous and oxidizer lead conditions; however, fuel leads resulted in lower reaction violence. The maximum overpressures measured for the 300-pound tests were equivalent to 2 pounds of TNT; for the 50-pound spill tests, 0.5

8.2 EXPLOSIVITY

Testing was conducted with laboratory quantities of N₂O₄ and the fuel blend (References 2 and 4) to determine whether or not propellant spills would lead to detonations. In Reference 39, S.S. Penner distinguishes between explosions and detonations as follows. In an explosion, the heat release rate and/or the number of molecules per unit volume increase with time more or less uniformly throughout a confined volume. A detonation wave, on the other hand, is spatially non-uniform and is propagated through unreacted combustible mixtures by an advancing shock front behind which exothermic chemical changes occur in such a way that the chemical heat released can be utilized to support further propagation of the detonation wave.

A closed chamber, approximately 1/150-scale version of the actual Titan II silo, was used for propellant spill tests (References 2 and 4). Spills were conducted with laboratory quantities of N₂O₄ and fuel blend at various mixture ratios with fuel leads and oxidizer leads. The largest quantity of combined propellants spilled into the chamber at a 2:1 mixture ratio was 0.1 pound (45 grams). At this mixture ratio, when 0.066 pound (30 grams) of N₂O₄ was added to 0.033 pound (15 grams) of fuel blend, an explosion occurred damaging the test chamber.

Based upon these tests, the following facts are presented:

- (1) Spillage of these propellants may cause explosions, but not detonations.
- (2) An increase in propellant quantity increases the reaction violence.
- (3) For the most part, spills are more reactive when fuel is added to the oxidizer than when the oxidizer is added to the fuel at identical quantities and mixture ratios.

Multiple spill tests were performed by Rocketdyne (Reference 40) on the Titan II propellants. Spills were conducted with 50 and 300 pounds of propellants in simulated Titan II open silos (1/10-scale and 1/18-scale versions). A 2-to-1 oxidizer-to-fuel ratio by weight was used on all tests. The following spill conditions were employed: simultaneous spills into a dry silo, oxidizer lead spills, fuel lead spill, and one simultaneous spill into water. Small-scale spills on dirt, water, and concrete also were conducted with 2.5 pounds of propellants. The data reported by Rocketdyne indicates that all explosions result from vapor phase reactions. In addition, the following information was reported:

- (1) Silo spills with fuel leads were less severe than with either the simultaneous or oxidizer leads. The simultaneous spills resulted in the most violent explosions.
- (2) Increase in propellant weight increased the reaction violence on spills made under simultaneous and oxidizer lead conditions; however, fuel leads resulted in a decrease in reaction violence. The maximum overpressures measured for the 300-pound spill tests were equivalent to 2 pounds of TNT; for the 50-pound spill tests, 0.2-pound of TNT.

SECTION 8.0
50/50 FUEL BLEND
AND N₂O₄

(3) The addition of water to the bottom of the silo reduced maximum temperatures and pressures resulting from the reaction of the propellants.

The Atlantic Research Corporation (Reference 25) reported two explosions when laboratory quantities of propellants were mixed. When 0.000 pound (2.7 grams) of 50/50 fuel blend was spilled onto 0.033 pound (15 grams) of N₂O₄, one explosion occurred during five tests; however, when 0.10 pound (4.5 grams) of N₂O₄ was spilled onto 0.006 pound of fuel blend, an explosion occurred for the one test. No pressure measurements were reported for any of these tests since the primary purpose of this work was to study control of fires involving N₂H₄-type fuels with air and N₂O₄.

8.3 REACTION PRODUCTS

During the spontaneous ignition temperature and flammability tests conducted by the U. S. Bureau of Mines, a dense white cloud of fine particles was formed when the vapors of the propellants react. The gaseous products obtained when N₂H₄ and UDMH vapors and an excess of N₂O₄ vapors combined were analyzed with a mass spectroscope. These gaseous products are shown in Table 8.1. An infrared absorption spectrum of the solids from both reactions also was obtained and the predominant structural groups and their corresponding wavelengths are given in Table 8.2.

No specific information is available concerning the products of combustion of the 50/50 fuel blend and the oxidizer. Only theoretical products can be predicted, such as carbon monoxide, carbon dioxide, water, nitrogen, and certain chemical radicals.

TABLE 8.1
MASS SPECTROSCOPE ANALYSES OF THE GASEOUS PRODUCTS
OF REACTION BETWEEN EXCESS N₂O₄ AND N₂H₄ AND
EXCESS N₂O₄ AND UDMH AT 20 mm OF Hg AND 77° F

Products	Reactants	
	N ₂ H ₄ (mole %)	UDMH (mole %)
N ₂ O	30	35
N ₂	38	34
H ₂ O	29	27
NH ₃	2	0
Hydrocarbons	--	4

TABLE 8.2

STRUCTURAL GROUPS ASSOCIATED WITH ABSORPTION PEAKS
IN THE INFRARED ABSORPTION SPECTRA OF THE
SOLID PRODUCTS OF REACTION BETWEEN N₂H₄ AND N₂O₄
AND BETWEEN UDMH AND N₂O₄ AT 22 mm OF HG AND 77°F

N ₂ H ₄		UDMH	
Wavelength (microns)	Structural Groups	Wavelength (microns)	Structural Groups
3.0	N-H (not H bonded)	2.8	OH
3.1	OH (H bonded)	3.2	NH, OH
6.3 }	N-H (bonding)	3.4	C-H
6.5 }		5.8	> C = O
		6.2	-COOH
		6.8	CH ₂ or CH ₃
		7.2	R ₂ N-N = O
		7.9	R ₂ N-N = O
		9.6	R ₂ N-N = O

SECTION 9.0

REFERENCES

SECTION 3.0

REFERENCES

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APPENDIX

VENDOR INDEX FOR NONMETALLIC MATERIALS

APPENDIX

VENDOR INDEX FOR NONMETALLIC MATERIALS

CERAMICS

Sauereisen 47, 31, and P-1
Temporell 1500

Sauereisen Cements Co., Pittsburgh, Pennsylvania
Not Known

GRAPHITES

Graphitar 2
Graphitar 50
Johns Mansville No. 60

U. S. Graphite Co., Saginaw, Michigan
U. S. Graphite Co., Saginaw, Michigan
Johns Mansville Co., New York, New York

PLASTICS

Armalon 7700, 7700B
Delrin
Fluorobestos
Fluorogreen
Garlock 900
Genetron GCX3B
Genetron XE2B
Hypalon 20
Kel-F 300
Kel-F (unplasticized)

DuPont, Wilmington, Delaware
DuPont, Wilmington, Delaware
Fluorocarbon Company, Fullerton, California
R. S. Hughes, Denver, Colorado
Garlock Packing Co., Culver City, California
Allied Chemical and Dye Corp., New York, New York
Allied Chemical and Dye Corp., New York, New York
Dow Corning Corp., Midland, Michigan
Minnesota Mining and Manufacturing Co.,
St. Paul, Minnesota
Minnesota Mining and Manufacturing Co.,
St. Paul, Minnesota

Lexan
Marlex 50
Marlex 5003
Moplen
Mylar
Nylon 31, 63, 101
Plexiglass
Polyethylene HD
Polyethylene (irradiated)

Dow Chemical Co., Midland, Michigan
Phillips Chemical Co., Bartlesville, Oklahoma
Phillips Chemical Co., Bartlesville, Oklahoma
Chemore Corp., New York, New York
DuPont, Wilmington, Delaware
DuPont, Wilmington, Delaware
Rohm and Haas Co., Philadelphia, Pennsylvania
Visking Corp., Chicago, Illinois
General Electric, Pittsfield, Massachusetts

PLASTICS (CONT)

Polypropylene	Campco Division, Chicago Molded Products, Chicago, Illinois
Raythene N	Ray Chem Corp., Redwood City, California
Saran	Dow Chemical Co., Midland, Michigan
Teflon Asbestos	Fluorocarbon Co., Fullerton, California
Teflon FEP	DuPont, Wilmington, Delaware
Teflon Graphite	Fluorocarbon Co., Fullerton, California
Teflon Molydisulfide	Fluorocarbon Co., Fullerton, California
Teflon TFE	DuPont, Wilmington, Delaware
Teflon TFE Felt 7550	DuPont, Wilmington, Delaware
Teslar 30	DuPont, Wilmington, Delaware
Trithene A	Visking Corp., Chicago, Illinois
Ultron	Monsanto Chemical Co., St. Louis, Missouri

BUTYL RUBBERS

Enjay	Enjay Co., Inc., New York, New York
268	Enjay Co., Inc., New York, New York
551	
Garlock 22	Garlock Packing Co., Culver City, California
Goshen 1357	Goshen Rubber Co., Inc., Goshen, Indiana
Hycar 2202	B. F. Goodrich Chemical Co., Cleveland, Ohio
Linear 7806-70	Linear, Inc., Philadelphia, Pennsylvania
Parco 805-70	Plastics and Rubber Products Co., Los Angeles, California
Parco 823-70	Plastics and Rubber Products Co., Los Angeles, California
Parker B496-7	Parker Seal Co., Cleveland, Ohio
Parker B480-7	Parker Seal Co., Los Angeles, California
Parker AB800-71	Parker Seal Co., Cleveland, Ohio
Parker 318-70	Hercules Facking Co., Lancaster, New York
Precision 9257	Precision Rubber Products Corp., Dayton, Ohio
Precision 9357	Precision Rubber Products Corp., Dayton, Ohio
Precision 214-907-9	Precision Rubber Products Corp., Dayton, Ohio
Stillman 613-75	Stillman Rubber Co., Culver City, California

FLUOROSILICONE AND FLUORORUBBERS

Fluorel	Minnesota Mining and Manufacturing Co., St. Paul, Minnesota
Hadbar 58789-23GT	Hadbar, Inc., Temple, California
Hadbar 58789-23	Hadbar Inc., Temple, California
Kel-F 3700, 5500	Minnesota Mining and Manufacturing Co., St. Paul, Minnesota
Parker 1235 Series	Parker Seal Co., Los Angeles, California
Parker V-494-7 (Viton B)	Parker Seal Co., Cleveland, Ohio
Silastic LS 53	Dow Corning Corp., Midland, Michigan
Silastic LS 63	Dow Corning Corp., Midland, Michigan
Stillman Rubber EX774-M-1 (Viton B)	Balanrol Corp., Niagara Falls, New York
Stillman ST 77-70 (Viton A)	Balanrol Corp., Niagara Falls, New York
Stillman TH 1057	Stillman Rubber Co., Culver City, California
TFNM-TFE	U. S. Army Quartermaster Research and Engineering Center, Natick, Massachusetts

POLYBUTADIENE RUBBERS

Acushnet	
SWK 849	
SWK 850	
SWK 851	
BWK 422	}
Stillman EX904-90 (Hydropol)	Acushnet Process Co., New Bedford, Massachusetts
	Stillman Rubber Co., Culver City, California

MISCELLANEOUS RUBBERS

Buna N	B. F. Goodrich Chemical Co., Cleveland, Ohio
Cohrlastic 500	Connecticut Hard Rubber Co., New Haven, Connecticut
Neoprene	Delta Products, Houston, Texas

PAINTS

Alkyd No. 4	Not Known
Catalac	Finch Paint and Chemical Co., Torrance, California
Chex-Wear	Benjamin Moore and Co., New York, New York
Co-Polymer P-200G	Co-Polymer Chemicals, Inc., Livonia, Michigan
Corrosite Clear 581	Corrosite Co., Chrysler Building, New York, New York
Epoxy 1, 5, 7, 9, and 6809	Not Known

PAINTS (CONT)

Floor Enamel 41138	Schutte and Co., Buffalo, New York
Primer MIL-P-6889	Not Known
Primer CA 9747	Sherwin Williams Co., Cleveland, Ohio
Tygon K	U. S. Stoneware, Plastics and Synthetic Division, New York, New York

COATINGS AND ADHESIVES

Armstrong A-3	American Cyanamid Co., Oakland, California
EC 847	Minnesota Mining and Manufacturing Co., St. Paul, Minnesota
HT 424	Not Known
Rockflux	Flexrock Co., Philadelphia, Pennsylvania

LUBRICANTS, GREASES, AND OILS

Andok C	Esso Standard Oil Co., New York, New York
DC 11	Dow Corning Corp., Midland, Michigan
DC 55	Dow Corning Corp., Midland, Michigan
DC High Vacuum Grease	Dow Corning Corp., Midland, Michigan
Drilube 703	Drilube Co., Glendale, California
Electrofilm 66C	Not Known
Halocarbon Grease	Halocarbon Products Corp., Hackensack, New Jersey
Kel-F 90	Minnesota Mining and Manufacturing Co., St. Paul, Minnesota
L 1111 Oil	Minnesota Mining and Manufacturing Co., St. Paul, Minnesota
LOX Safe	Redel Corp., Anaheim, California
Microseal 100-1, 100-1 CG	Microseal Products Sales, Torrance, California
Molykote Z	Alpha Molykote Corp., Stamford, Connecticut
Nordoseal 147, 421	Rockwell Manufacturing Co., Pittsburgh, Pennsylvania
Polyglycol Oils	Dow Chemical Co., Midland, Michigan
QC-2-0093	Not Known
QC-2-0026	Not Known
Rayco 30 and 32	Not Known
Rockwell-Nordstrom No. 950	Rockwell Manufacturing Co., Pittsburgh, Pennsylvania

LUBRICANTS, GREASES, AND OILS (CONT)

S#58-M Oil	New York and New Jersey Lubricating Co., New York
TMSF 1, 2, 3	Not Known
UDMH Lube 50/50 Mixture of UDM Lube and Electro Mechanics No. 20057	Superlube, Inc., Cleveland, Ohio
Vydex A	Electro Mechanics Inc., New Britain, Connecticut
	DuPont, Wilmington, Delaware

THREAD SEALANTS AND POTTING COMPOUNDS

Crystal M and CF	Not Known
Epon 828	Shell Chemical Co., San Francisco, California
Fairprene 5159	Not Known
N ₂ O ₄ Sealant	Redel Corp., Anaheim, California
Paraplex P-43	Not Known
Proseal 793	Coast Proseal and Manufacturing Co., Los Angeles, California
PR 1422	Products Research Co., Burbank, California
Reddy Lube 100, 200	Redel Corp., Anaheim, California
RTV 20	General Electric Co., Pittsfield, Massachusetts

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